

**ISTANBUL TECHNICAL UNIVERSITY ★ GRADUATE SCHOOL OF
SCIENCE ENGINEERING AND TECHNOLOGY**

**MODELLING THE FATE OF PARTICULAR COMPONENTS IN AEROBIC
SLUDGE STABILIZATION FOR ALKALOID WASTEWATER USING
MEMBRANE BIOREACTOR**

M.Sc. THESIS

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**ALKALOİD ATIK SUYUNUN MEMBRAN BİYOREAKTÖR İLE
ARITILMASIYLA OLUŞAN ATIK ÇAMURUN AEROBİK ÇAMUR
STABİLİZASYONUNDA PARTİKÜLER BİLEŞENLERİN MODELLENMESİ**

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ABBREVIATIONS

COD	: Chemical Oxygen Demand
BOD₅	: Biochemical oxygen demand
F/M	: Food to Microorganism Ratio
SS	: Suspended Solids
VSS	: Volatile Suspended Solids
SRT	: Sludge Retention Time
OUR	: Oxygen Uptake Rate
MLVSS	: Mixed liquor volatile suspended solids
OLR	: Organic loading rate
TS	: Total solids
TSS	: Total suspended solids

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MODELLING THE FATE OF PARTICULAR COMPONENTS IN AEROBIC SLUDGE STABILIZATION FOR ALKALOID WASTEWATER USING MEMBRANE BIOREACTOR

SUMMARY

Industrial wastewater includes high amount of sulphate, acetic acid and organic matter due to the process of Alkaloid. Alkaloid wastewater that is used in this study has already been treated in a pilot scaled reactor according to the decharge standarts in legal regulations to execute a sustainable wastewater treatment. The industrial plant, which is studied, has an avarage flow rate of 480 m³/d and a maximum chemical oxygen demand (COD) concentration of 43000 mg/L. COD parameters must be increased to 170 mg/L as proposed in the Turkish Water Aquaculture Regulation (1995). However; because it seems unachievable to reduce the concentration, 1500 mg/L which is indicated in the Turkish Water Control Regulation (2004) was taken into consideration. Thus 99.6 percent of COD removal efficiency becomes obligatory to achieve the discharge limit after the treatment (Keskinler and İnsel, 2014).

Sludge management is one of the most critical environmental issues all over the world due to the population expansion and the increase in the number of the wastewater treatment plants. Appropriate sludge management requires the selection of the economically feasible as well as the suitable disposal methodology especially for sludges generated from industrial wastewater treatment plants that contain significant amount of pollutants.

During the adaptation period of European Union membership of Turkey, the increase in the number of both municipal and industrial Wastewater Treatment Plant (WWTP) due to the stringent new regulations for wastewater treatment will pose more significant sludge disposal and sanitation problems in the future for Turkey. Treatment and ultimate disposal of domestic and industrial wastewater treatment plant sludges is obligated according to the regulations in Turkey.

The principal objective of sludge treatment is its stabilization, that is a controlled decomposition of easily degradable organic matter resulting in a significant reduction of volatile suspended solids (VSS) content, a change of an unpleasant smell into an earthy one, and an elimination of sludge putrescibility.

Aerobic biological stabilization at ambient conditions has traditionally been undertaken for the stabilization of treatment sludges originated from both domestic and industrial wastewater treatment plants.

This thesis study aims to identify the dissolved and inert particulate component concentrations of influent wastewater, which resulted from alkaloid process within the contex of biologic treatability-based concentration. Aerobic stabilization of sludge in the pilot scaled membrane bioreactor, in which the wastewater was treated, was evaluated and the endogeneous decay coefficient was determined as respirometric. With the help of respirometric experiments and modelling kinetic and

stoichiometric coefficients that related to biologic system were detected. Furthermore, particular product concentration of the sludge and decay coefficients were detected through modelling by using all of the results.

To determine the particulate inert and dissolved substances in the influent wastewater (Orhon et al., 1994) method was used. According to this method 2 reactors, which were continuously aerated and were fed with raw wastewater, soluble wastewater were operated. According to experimental results of initial wastewater characterization, inert COD X_I and S_I were calculated as 309 mg/L (1.13 % of the C_T) and 416 mg /L (1.52 %).

Sludge that includes 23000 mg SS/L and 9800 mg/L VSS were used in the process of Aerobic Stabilization. SS, VSS and pH measurements were made timely and daily. The experiment had been carried on until the SS/VSS parameters were stabilized. The VSS/SS ratio of the stabilized sludge was found 0.35 mg VSS/mg SS. External aerobic sludge stabilization of the thickened sludge achieved a volatile suspended solids reduction % 38 after 19 days.

The determination of the kinetics of decomposition of alkaloid wastewater and aeration system design-related parameters to determine respirometric techniques are widely used. (Insel et al., 2003; Cokgor et al., 2008). It was observed that when wastewater is added on biomass in an aerobic environment, OUR level increases rapidly from 35 mg O_2 /L/hour to 365 mg O_2 /L/hour in a couple of minutes. Oxygen used per a unit of MLSS could be calculated as 126 mg O_2 /L/g MLSS/hour. It can be understood from the respirometric profile that 85 percent of the organic material in raw wastewater is readily biodegradable and it is not inhibited in an aerobic environment.

Application of the method proposed by (Ekama et al., 1986) based on successive measurements of descending OUR levels in the course of sludge stabilization yielded endogenous decay rate (b_H) of 0.14/d.

AQUASIM simulation program was used in the modelling processes. Decay of the particulate substance study was based on (Özdemir et al., 2014). OUR data were simulated using the Activated Sludge Model No:1 (ASM1), which provides a mechanistic description for this process is adopted in this part of the study. Biomass composition assessed by model calibration involves four major fractions, namely heterotrophic active biomass, X_H ; remaining particulate slowly biodegradable COD, X_S ; particulate inert COD of influent origin, X_I and particulate metabolic products, X_P generated in the course of metabolic reactions in the reactor. The modelling experiments indicates a total solids concentration of mg COD/L when expressed in terms of cell COD, corresponding to a VSS value of 2375 mg/L; the corresponding active biomass (X_H) level is around 2854 mg COD/L. The model estimated the hydrolysis rate constant for X_P (K_{XP}) as 0.01 mg COD/mg COD.

Finally the effects of sludge retention time (SRT) of the activated sludge process on sludge composition and aerobic sludge stabilization was searched for. In terms of Özdemir et al., 2014, Activated sludge processes operated at different sludge ages have different K_{XP} . K_{XP} value increased with increasing SRT.

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ÖZET

Alkaloid prosesinden kaynaklanan endüstriyel atıksular yüksek sülfat, asetik asit ve organik madde içermektedir. Bu çalışmada kullanılan alkaloid atıksuları su geri kazanımının sağlanması, mevzuatta yer alan deşarj standartlarına uygun olarak sürdürülebilir atıksu arıtımının gerçekleştirilmesi amacıyla hali hazırda pilot ölçekli bir membran biyoreaktör ile arıtılmaktadır. İncelenen endüstriyel tesisin ortalama debisi 480 m³/gün ve kimyasal oksijen ihtiyacı (KOİ) konsantrasyonu maksimum 43000 mg/L'dir. KOİ parametresinin Su Ürünleri Yönetmeliği (1995)'nde öngörülen 170 mg/L'ye kadar indirilmesi gerekmektedir. Fakat konsantrasyonu bu değere indirmek mümkün olmadığından Su Kirliliği Kontrol Yönetmeliği (2004)'nde belirtilmiş olan 1500 mg/L baz alınmıştır. Buna göre, deşarj limitinin sağlanması için arıtma sonrasında %99.6 KOİ giderim verimi elde edilmesi zorunlu olmaktadır (Keskinler ve İnel, 2014).

Çamur yönetimi, atık su arıtma tesislerindeki artış ve nüfustaki genişleme yüzünden dünya üzerindeki en önemli konulardan biri haline gelmiştir. Uygun çamur yönetimi sağlayabilmek için ekonomik uygulanabilirlik kadar, kayda değer sayıda kirliliğe sebep olan maddeler içeren endüstriyel atık su arıtma tesisi kaynaklı çamurların da imhası sağlanabilmelidir.

Türkiye'nin Avrupa Birliğine uyum sürecinde, hem belediyelerin hem de endüstrinin atık su arıtma tesislerindeki artış katı yönetmelikler sebebiyle sanitasyon ve çamurun imhası konularında Türkiye'ye ciddi sorunlar yaşatacaktır. Yerel ve Endüstriyel atık su arıtma tesislerindeki artıma ve nihai çamur imhası Türkiye'deki yönetmelikler esas alınarak yapılmaktadır.

Çamur arıtmasının temel ilkesi stabilizasyondur ki bu da uçucu askıda katı maddelerin (UAKM) içeriğinden kaynaklanan kolay parçalanabilir maddelerin kontrollü ayrıştırılması, kötü kokuların yok edilmesi ve çürüyen çamurun yok edilmesiyle sağlanmaktadır.

Bu tez çalışmasında alkaloid prosesinden kaynaklanan giriş atıksuyunun biyolojik arıtılabilirlik bazlı karakterizasyonu kapsamında inert partiküler ve çözünmüş madde konsantrasyonlarının belirlenmesi hedeflenmektedir. Oluşan atıksuların arıtıldığı pilot ölçekli membran biyoreaktörde oluşan atık çamurun aerobik stabilizasyonunun değerlendirilmesi yapılmış olup içsel dönüşüm katsayısı respirometrik olarak belirlenmiştir. Respirometrik deneyler ve modelleme yardımıyla biyolojik sistem ile ilgili kinetik ve stokiyometrik katsayılar bulunmuştur. Ayrıca elde edilen tüm sonuçlar kullanılarak biyolojik çamurun partiküler ürün konsantrasyonu ve bu partiküler ürünün ayrışma katsayıları da modelleme ile belirlenmiştir.

Giriş atıksuyunda çözünmüş ve partiküler inert maddelerin belirlenmesi için Orhon ve diğ., 1994 yöntemi kullanılmıştır. Bu yöntem gereğince aerobik işletilen ve toplam ve çözünmüş ile beslenen 2 adet reaktör kurulmuştur. Deney sonuçlarına göre, toplam KOİ miktarı 27344 mg/L olan giriş alkaloid atık suyunun % 1.13'ü yani toplam partiküler inert madde miktarı 309 mg/L, % 1.52'si yani toplam çözünmüş inert madde miktarı 416 mg/L olarak belirlenmiştir.

Aerobik çamur stabilizasyon prosesinde 23000 mg/L AKM ve 9800 mg/L UAKM içeren atık çamur kullanılmıştır. Zamana karşı günlük bazda AKM, UAKM ve pH ölçümü yapılmıştır. Deney AKM/UAKM parametreleri sabitlenene kadar devam etmiştir. Deney sonunda UAKM/AKM oranı 0.35 mg UAKM/mg AKM bulunmuştur. 19 gün sonunda giderim verimi % 38 UAKM olarak hesaplanmıştır.

Alkaloid atık suyunun ayrışma katsayılarının ve havalandırma sisteminin dizayn parametrelerinin (ayrışma kinetiği tespiti, havalandırma sistemi tasarımı) belirlenmesi için respirometrik teknikler yaygın olarak kullanılmaktadır. MBR pilot ünitesinden alınan aktif çamur numunesi, İTÜ Çevre Mühendisliği, Sedat Üründül Biyoteknoloji Laboratuvarı'na ulaştırılarak tamamen oksijenli ortamda biyokütle aktivite testine tabi tutulmuştur. Biyokütle, Applitek RA-1000 tipi sürekli respirometre hücresine konularak üzerinde Alkaloid ham atıksu ilavesi (100 mL Giriş KOİ: 31,000 mg/L) gerçekleştirilmiş ve zamana karşı Oksijen Tüketim Hızı (OTH) dakikada bir frekansta kaydedilmiştir. Atıksu biyokütle karışımı pilot arıtma tesisindeki F/M (Food/Microorganism=0.25 kgKOİ/kgMLSS/gün) oranını yansıtacak şekilde seçilmiştir. F/M oranını ayarlayabilmek için de MBR çamuru pilot MBR permeat suyu ile 2900 mgMLSS/L seviyesine ayarlanmıştır. (Insel ve diğ., 2003; Cokgor ve diğ., 2008). Aerobik koşullarda biyokütle içerisinde alkaloid atıksuyunun eklenmesiyle başlangıçta oksijen tüketim hızı (OTH) seviyesi 35 mg O₂/L/saat iken birkaç dakika içerisinde 365 mgO₂/L/saat seviyesine yükselmiştir. MLSS konsantrasyonu başına kullanılan oksijen miktarı ise 126 mg O₂/L/saat olarak hesaplanır. Çamur bekletme süresi 20 gün olan atıksuyundan elde edilen respirometrik profilden yararlanılarak, atık suundaki organik maddenin %85'inin kolay ayrışabilir madde olduğu anlaşılmaktadır. Kolay ayrışabilir maddeler aerobik koşullarda inhibe olmamaktadırlar. Kolay ayrışabilen organik maddenin yüksek olmasının sebebinin üretimde kullanılan asetik asit vb. maddelerden kaynaklandığı şeklinde yorumlanabilir. Ayrışabilen organik maddenin tamamı 400 dakika reaksiyon süresi sonunda tükendiği rapor edilmektedir.

Aerobik stabilizasyon çalışmasında oksijen tüketim hızına bağlı olarak ölçülen içsel solunum hızı (b_H) Ekama ve diğ., 1986 tarafından önerilen methodu baz alınarak 0.14/gün olarak hesaplanmıştır.

Modelleme çalışmalarında AQUASIM simülasyon programı kullanılmıştır. Partiküler ürünün ayrışma çalışması Özdemir ve diğ., 2014 çalışması baz alınarak yapılmıştır. Ayrıca stabilizasyon sürecinde elde edilen OUR profilleri Aktif Çamur Modeli No:1 (ASM1) kullanılarak modifiye edilmiştir. Reaktörde biyokütle içeriği aktif heterotrofik biyokütle X_H, yavaş ayrışan partiküler biyokütle X_S, partiküler inert madde, X_I ve metabolik reaksiyonlar sonucu oluşan X_P olarak dört ana bileşen model kalibrasyonu ile değerlendirilmiştir. Model çalışmalarında 4063 mg COD/L olan toplam biyokütle miktarı içerisinde heterotrofik biyokütle miktarı KOİ cinsinden ise 2854 mg KOİ/L olarak belirlenirken UAKM cinsinden 2375 mg UAKM/L olarak hesaplanmıştır. Model aynı zamanda X_p için hidroliz hız sabitini (k_{XP}) 0.01 mg KOİ/mg KOİ olarak vermiştir.

Son olarak amur yařının aktif amur prosesinde amur bileřenlerine etkisi arařtırılmıřtır. Bu baėlamda kullanılan zdemir ve diė., 2014 alıřmasında, aktif amur prosesi farklı amur yařlarında stabilize edilmiřtir. amur yařı arttırıldığında k_{XP} deėerinin arttıėı gzlemlenmiřtir.

1. INTRODUCTION

Opium is a product which is known traditionally in Turkey and its plantation and harvesting is controlled by the Government (Sevimli *et al.*, 1999).

Opium alkaloid plant has a mean flow rate of 27.5 m³/hr and it produces 480 m³/day wastewater (Sevimli *et al.*, 1999). The Factory is draining its effluent to Eber Lake by Akarçay River. The Lake's contamination is a threat not only to bird and fish species which have this territory as their habitat, but also to humans living in whereabouts. Wastewaters of sugar, cement and other factories besides alkaloid industry, are also drained to Eber Lake and this is increasing the contamination rate in the lake.

Information on characteristics, treatment and disposal of effluents from opium alkaloid industry is quite limited since cultivation and processing of opium is not practiced in most of the developed countries. Hence, only limited information can be found in scientific literature about the characterization and treatment of opium alkaloid industry wastewater.

The disposal and handling of excess sludge has been a rising problem for wastewater treatment plants worldwide. The cost of sludge disposal have increased substantially in the last decade and the management and treatment of the excess sludge represents more than 50% of the construction and operating costs of wastewater treatment plants (Metcalf and Eddy, 2003). Therefore the optimization of the sludge disposal is crucial and a sustainable option for the long-term management of the sludge must be environmental friendly, feasible and economically viable. Conventional sludge disposal methods are strictly regulated in many countries since they may cause secondary pollution problems and encounter strong public opposition due to reduced land availability as well as leachate and greenhouse gas emission concerns (Wang *et al.*, 2008; Do *et al.*, 2009).

In this context, experimental and modelling studies were conducted to characterize stabilization of biological sludge under aerobic conditons.

1.1 Aim and Scope of the Thesis

The aims of this study are to determine the characterization of opium industry wastewater and to investigate the treatability of this effluent by aerobic processes. Aerobic sludge stabilization in membrane bioreactor and endogenous decay coefficients by respirometric analysis are also determined.

In the scope of the thesis, the following steps were performed:

- The wastewater used in this study was obtained from the influent of existing Turkish Grain Board (TMO) Afyon Alkaloid Industry Wastewater Treatment Plant. Sludge subjected to aerobic stabilization for about 20 days and conventional methods, oxygen uptake rate(OUR) measurements and molecular analyses were used to investigate efficiency of stabilization.
- The role of endogeneous decay and microbial activity in aerobic stabilization of biological sludge were estimated. The evaluation included two different respirometric procedures based on decrease of endogeneous respiration and loss of microbial activity.
- Dissolved and inert particulate component concentrations of influent wastewater, which resulted from alkaloid process within the context of biologic treatability-based concentration were identified.
- Modelling studies were conducted to stimulate VSS concentration and fate of particular components during aerobic stabilization.
- Modelling studies were also conducted to stimulate OUR profiles obtained during stabilization period.

2. LITERATURE REVIEW

2.1 Alkaloids

Alkaloids are chemical substances functioning as amines which have one or more nitrogen atoms and usually contained in a heterocyclic ring system. Mostly plants produce alkaloids and many of them are active on animals pharmacologically and so on the humans that eat them, affecting the nervous system and other essential processes. Some insects use alkaloids for their defense systems to create toxic against predators because they are immune to the effects of toxic. Major alkaloids' chemical structures examined in this thesis are shown in Figure 2.1 (Crews, 2014).

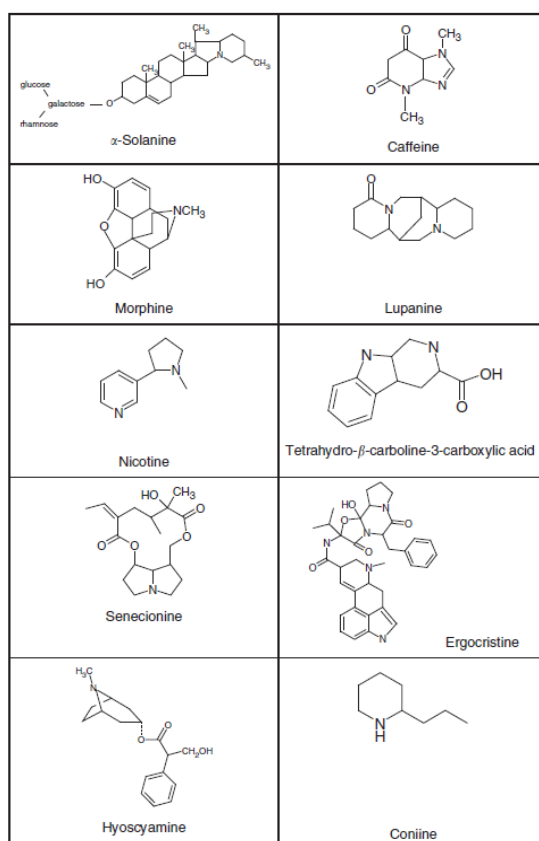


Figure 2.1: Chemical structures of some common alkaloids (Crews, 2014).

2.2 Opium Alkaloid Industry

2.2.1 Process description

Opium, which is used for medical purposes both in Turkey and in the world, is obtained from the plant, opium poppy (*Papaver somniferum* L.) The planting of opium poppy is supervised by the UN all over the world. The UN designated Turkey, India, Australia, France, Spain, Hungary, Czech Republic and China as the legal producers of opium poppy (Arslan et al., 2008).

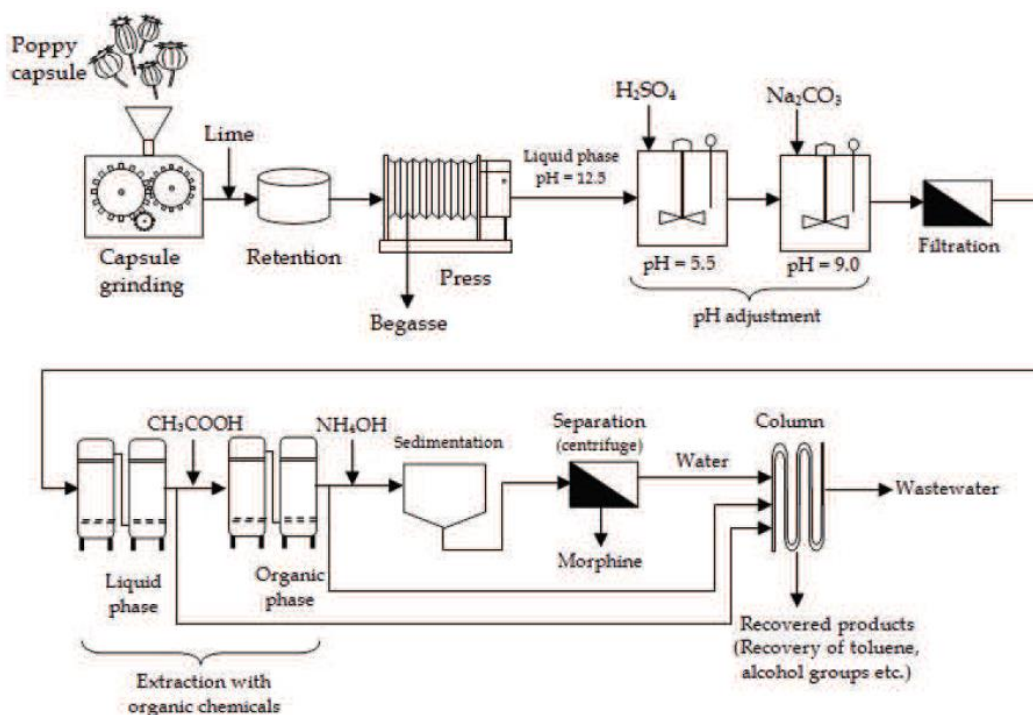


Figure 2.2: Process flow diagram for an opium alkaloid industry (Erşahin et al., 2011).

Opium contains approximately 26 different kinds of alkaloids like morphine, narcodine, codein, papavarine and thebain (Sevimli et al., 1999). Different kinds of methods can be used to extract alkaloids from natural raw materials. Mostly these methods are based on both the alkaloid solubility in organic solvents and the solubility of their salts in water (Hesse, 2002). The flow of the transaction plan of a wet-mill opium alkaloid industry, which is mostly based upon grinding, solid-liquid and liquid-liquid extraction and crystallization processes, was given in Fig. 2.2 (Erşahin et al., 2011).

After grinding and treating opium poppy capsules with an alkaline solution (lime), the sludge is being pressed to obtain the liquid which has the alkaloids inside. The pH of this liquid is altered to 9,0 and the filtration helps to separate the contamination. The alkaloids' extraction is being processed by organic materials like toluene, butanol and by acetic acid. Ammonium crystallize the morphine and separates it from the solution through centrifuges. Solvents which are used in the process and the water are distilled in the column with the aim of recovery of the products such as toluene, alcohol groups etc. and then the wastewater is treated in the plant (Sevimli et al., 1999).

The Alkaloid Factory in Afyon's Bolvadin territory was authorized in 1980. 75 tons of morphine is produced in each year in the factory. The Ministry of Agriculture is the owner of this factory. In 2003 Turkey cultivated 100,000 hectares and yielded 145 tons of CPS (M) approximately the 30% of the global morphine production. It is estimated that Turkey profits \$60 million yearly from the exportation of poppy seeds and morphine (Gecin and Hakbilen, 2005).

The process plan of the plant is illustrated in Figure 2.2. There are two sectors in the factory. One of them is the extraction unit, which operates continuously and extracts the resin from plants with the concentrated poppy straw method. In the other sector different drugs are obtained from the raw product by mixing and reacting with chemicals (Kunukcu *et al.*, 2004). The chemicals used in the process of extraction are given in Table 2.1.

Table 2.1: Chemicals used during extraction and their amounts (Aydın, 2002)

Name of chemical used	Amount of chemical used (kg/tons capsule)
Lime	92.5
Toluene	7.5
Sodium carbonate	94.6
Acetic acid	22.3
Sulphuric Acid	48.3
Ammonia (%25)	5.6
Butanol	5.1
Caustic	1.1

2.2.2 Sources of wastewater and characteristics of opium alkaloid waste effluents

There are four main units (Grinding, liquid-solid, liquid-liquid extraction and crystallisation) in an opium alkaloid processing plant.

Grinding unit: In this unit, the capsule of opium is separated from contamination and is ground for the later usage in the liquid-solid unit.

Liquid-solid extraction process: The lime solution is mixed with ground capsules and this mixture is pressed for the extraction of morphine. The extract includes adjusted pH of 9 is separated cleanly.

Liquid-liquid extraction process: Opium contains approximately 26 different kinds of alkaloids like morphine, narcodine, codein, papvarine and thebaine. These are extracted on commercial based scale. The degradation and processing of alkaloids includes extraction of opium with acetic acid at pH 5.0. The aqueous extract is processed with organic solvents like toluene and butanol in forward.

Crystallization process: In this process, morphine is separated from acetate solution by ammonia solution and the it is centrifuged and dried.

The plant is able to produce 72 tons of opium daily, and 3.3 kg of morphine can be obtained per ton of opium processed. The 9.2 m³ of water can be consumed per ton of opium processed. The average of 480 m³/day effluent can be generated from the extracion of alkaloid. The wastewater production is spesifically about 6.7 m³ for a ton of opium capsule. The wastewater flows as 27.5 m³/hr avaragely. Nowadays the plant operates 5 days in a week; yet, it is being studied to operate the plant 7 days a week so that it can process more opium (Sevimli et al., 1999).

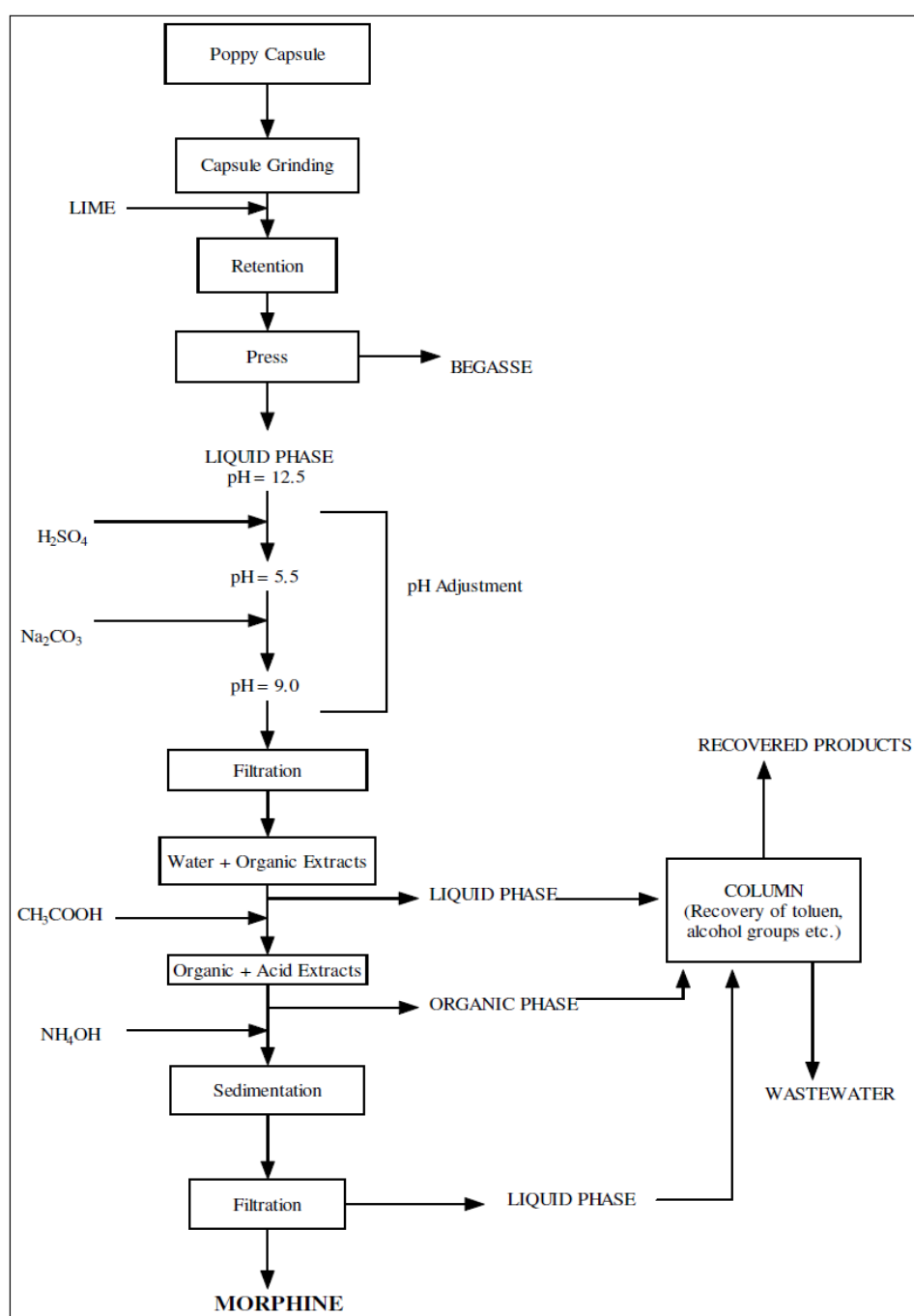


Figure 2.3: Afyon Alkaloid Factory production flow scheme (Aydın, 2002).

2.2.3 Performance evaluation of the existing wastewater treatment plant

The treatment plant is designed to treat 660 m³ per day. 480 m³ of it is sourced from opium alkaloid manufacturing and 180 m³ from domestic uses. The treatment includes a 2-stage activated sludge system Fig. 2.4. The volume of aeration basins in both stages are 2632 m³ and the volume of the settling tanks are 153 m³. The diameter of settling tanks in both stages are 8 m. Phosphoric acid is added to wastewater so that it can provide enough phosphorus in the aeration basins.

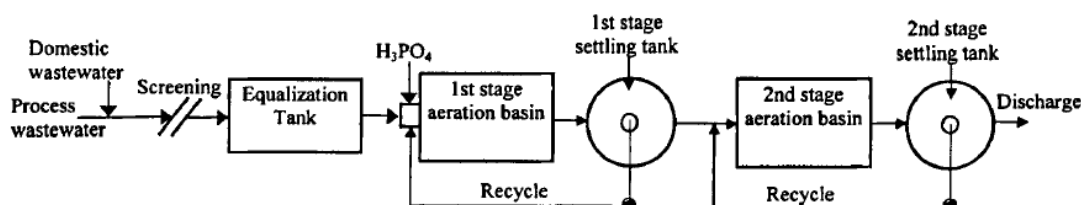


Figure 2.4: Flow diagram of two stage opium alkaloid wastewater treatment plant (Sevimli et al., 1999).

2.3 Opium Alkaloid Wastewater

Opium alkaloid industry releases dangerously contaminated wastewaters that includes high concentrations of COD (mainly soluble), BOD₅ and TKN, dark brown colour and low pH. Alkaloid industry wastewaters are lack of phosphorus in general; thus for biological treatment addition of phosphorus is highly needed. The wastewater may include up to 90% of soluble COD content and up to 33% of acetic acid related COD (Aydin et al., 2010). The initial soluble inert COD in opiumalkaloid industry wastewater was calculated as 2% by Sevimli et al. (1999). Aydin et al. (2010) stated the initial soluble and particulate inert COD content of opium alkaloid industry wastewaters under anaerobic conditions as 1,64% and 2,42%, respectively. Even if there is not enough data on the sulphate content of the alkaloid industry wastewaters, it might be thought that it includes high concentrations because of the sulphuric acid addition in the pH adjustment part. Ozdemir (2006) stated a sulphuric acid usage of 48,3 kilograms for each ton of opium. Moreover, the alkaloid wastewaters may also contain some toxic organic chemicals inhibited in biological treatments like N,N-dimethylaniline, toluene (Aydin et al., 2010). Table 2.2 presents the common characteristics of opium alkaloid industry effluents.

Table 2.2: Characteristics of opium alkaloid industry effluents (Erşahin, 2011)

Parameter	Unit	Reference					
		Bural et al. (2010)	Aydin et al. (2010) ¹	Ozdemir (2006)	Sevimli et al. (1999)	Timur & Altinbas (1997)	Deshkar et al. (1982)
COD	mg/L	30000-43078	18300-42500(25560)	22000-34780	36500	21040	18800
Soluble COD	mg CaCO ₃ /L	28500-40525	17050-39470	-	-	-	-
BOD ₅	mg/L	16625-23670	4250-22215(12000)	21250	32620	12075	15000
Alkalinity	mg/L	-	315-4450 (1290)	144-1050	-	4450	-
pH	-	4,5-5,36	4,9-6,3 (5,4)	-	4,95	5,1	8,4
TKN	mg/L	396-1001	550-841(673)	1001	1030	380	1870
NH ₃ -N	mg/L	61,6-259	73-141(98)	61,6-172,5	140	110	35
TP	mg/L	4,0-5,21	3,1-15,0	4-5,21	65	2,0	1,3
TS	mg/L		27235-29750	-	-	27235	15475
TSS	mg/L	555-2193	565-2295	1120-1700	1400	1005	38
TVS	mg/L	382-1395	320-1775	580-990	-	805	-
Color	Pt-Co	4375-4750 ²	2150-2550	4750	-	-	-

1 Numbers in parenthesis represent the median values.

2 After coarse filtration

Approximately 2% of alkaloid wastewater COD was found to be inert (Sevimli *et al.*, 2000). Discharge standards for this industry, in fact for only this factory is presented in Table 2.3.

Table 2.3: Alkaloid production plant wastewater discharge standards (*)

Parameter	Unit	Composite Sample (24 hr)
COD	(mg/L)	1500
TKN	(mg/L)	15
TSS	(mg/L)	200
pH	-	6-9

(*) Turkish Water Pollution Control Regulation, 2004, Table 14.17.

Table 2.4: Characteristic of opium alkaloid wastewater (Özdemir, 2006.)

Parameter	Unit	Value
pH	-	4.5-5.2
Total COD	mg/L	22000-34780
BOD ₅	mg/L	21250
TSS	mg/L	1120-1700
VSS	mg/L	580-990
TKN	mg/L	1001.2
NH ₄ -N	mg/L	61.6-172.5
Total P	mg/L	4-5.21
Alkalinity	mg/L as CaCO ₃	144-1050
Color	Pt-Co	4750
Protein	mg/L	5330
Carbohydrate	mg/L	10000

There is a wastewater treatment plant which has a serial activated sludge systems with diffusers. In the beginning COD removal efficiencies were able to be obtained up to 90-95 % but, because of several operational issues and high costs of aeration, the plant is no more operating effectively. The flow scheme of the existing treatment plant is given in Figure 2.5. The vital operating issue was the noncontrollable increase of heat in the aeration basins and this was mostly because of the cover effect of the thick scum layer and a long hydraulic detention time (Sevimli *et al.*, 2000).

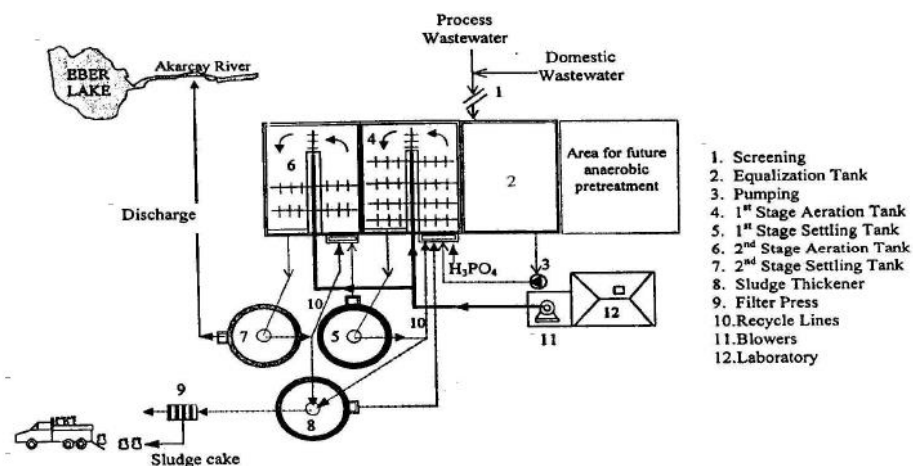


Figure 2.5: Flow scheme of existing wastewater treatment plant (Sevimli *et al.*, 2000).

2.3.1 Previous treatability studies on opium alkaloid wastewater

Most of the treatment studies, performed on alkaloid wastewater, in literature were carried out İstanbul Technical University (İTÜ) and TÜBİTAK Marmara Research Center (MAM). These studies contains not only the treatability of raw wastewater but also the effluent released from existing wastewater treatment plant. Previous treatability studies on opium alkaloid wastewater are summarized in Table 2.5 and described below:

2.3.1.1 TÜBİTAK Marmara Research Center (MAM) studies (Kınlı, 1994):

These studies were applied to effluent of WWTP. They can be classified as physicochemical treatment (alum, FeCl_3 , $\text{Fe}_2(\text{SO}_4)_3$), adsorption studies (activated carbon, perlite, cement powder) and chemical oxidation (potassium permanganate, hydrogen peroxide). The most significant results obtained were alum, $\text{Fe}_2(\text{SO}_4)_3$ and potassium permanganate oxidation which resulted in COD removals around 43-45% by a concentration of 1000 mg/L. Initial COD values were not given for wastewater used in this study.

2.3.1.2 Anaerobic treatability studies (Sevimli et al., 2000):

A 36 L of UASB pilot reactor's operation process took about 5 months. The seed was obtained from İzmit PAKMAYA wastewater treatment plant. The initial COD which was fed to the reactor was recorded between 7000 and 13000 mg/L which was about 0.25-0.4 of the original COD of alkaloid wastewater. The efficiency of removal was between 50-75 %. Moreover anaerobic studies which were performed with alkaloid wastewater showed initial COD values of 8000-16000 mg/L. In these studies obtained COD removal efficiencies were about 62-90%. The results are shown in Table 3.4.

The mesophilic treatment of opium alkaloids effluents of industry was searched for by a pilot scale UASB reactor (36 L) which was operated at a variety of OLRs (2,8 – 5,2 kg COD/m³.day) and at a HRT of 2,5 days by Sevimli et al. (2000) Some operational problems were experienced through the operation period but 50-75% efficiency of COD removal was achieved eventually. Aydın et al. (2010) put forward one of the most elaborated and continuous work on the anaerobic treatability of effluents generated from an opium alkaloids industry.

Lab-scale UASB reactor's (11,5 L) treatment capability was experimented in mesophilic conditions and under various HRTs (0,84–1,62 days) and OLRs (3,4–12,25 kg COD/m³.day). However, efficiency of the COD removal slenderly diminished with increasing OLR and decreasing HRT, the reactor showed high COD removal efficiencies altered between 74%–88%. Moreover, an ascetic suppression caused by N,N-dimethylaniline in the wastewater, that came up in the sterilisation operation at the derivation unit tanks of the industry, was appeared in the study. Through the inhibition period, efficiency of the treatment and output of biogas fell down immediately, though the OLR was decreased and HRT was increased as a contraceptive action. These intercessions couldn't help and performance of the reactor didn't improve so new sludge had to be placed for four months because of the irreversible inhibition. New sludge helped the reactor to reach the same efficiency level easily at each time. Average methane yield of the opium alkaloids industry wastewater was reported as 0,3 m³ CH₄/kg COD removed. Anaerobic Digestion Model No.1 (ADM1) was applied by Dereli et al., (2010), IWA Task Group (Batstone et al., 2002) evolved an integrated model, for the details acquired by Aydin et al. (2010). ADM1 had the chance to simulate the UASB reactor performance according to effluent COD and pH, on the contrary some discrepancies were experinced for methane gas previsions. Özdemir (2006) was searched for the co-digestion of alkaloid wastewater with acetate/glucose by batch testings, consequently the usage of these co-substrates weren't able to improve removal efficiency remarkably but adaptation period of microorganisms was decreased. Constant anaerobic treatment of alkaloid industry wastewater was investigated forwardly by Ozdemir (2006) benefiting from three lab scale UASB reactors (Reactor 1: fed with alkaloid wastewater after hydrolysis/acidification, Reactor 2: fed with raw alkaloid wastewater, Reactor 3: fed with alkaloid wastewater together with sodium acetate as co-substrate) performed at various OLRs (2,5–9,2 kg COD/m³.day) and a HRT of 4 days. Even though all of the reactors processed comfortably at low OLRs (~80% COD removal efficiency), in R1 and R2 reactors at the OLR of 9,2 kg COD/m³.day some failures were experienced. Ozturk et al. (2008) worked on the anaerobic treatability of the mixture of wastewater generated from the distillation column and domestic wastewater of an alkaloid industry by a full-scale anaerobic Internal Cycling (IC) reactor with an OLR of 5 kg COD/m³.day. Efficiencies of COD and VFA removal 85 and 95%, severally. Obtained rate of biogas

production was 0,1- 0,35 m³ CH₄/COD removed. Higher salinity and sulphate concentrations were the main problems of this study.

In the aim of submitting the competency of the anaerobic treatment, a pilot plant was built and worked since July 1997 under the field states. The anaerobic reactor was set up as an Upflow Anaerobic Sludge Blanket Reactor (UASBR). The amount of the reactor is 36 litres. The pilot plant processed in the study is ornamented in Figure 2.6.

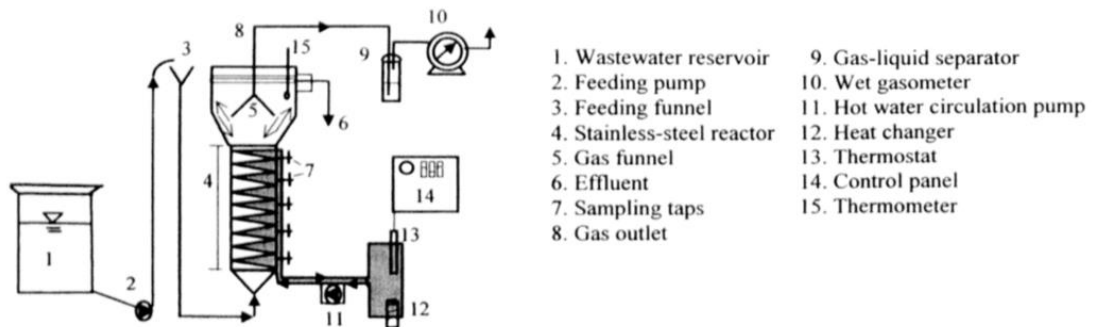


Figure 2.6: Schematic of the UASBR. (Sevimli et al., 1999)

2.3.1.3 Ozone oxidation (Sevimli *et al.*, 2000):

Ozone oxidation was executed on outflow from WWTP. Optimum removal of COD was achieved at pH 2.5 for 40 minutes of ozonation which occurred to be 43%. Initial COD rates were not stated for wastewater used in this work.

The experimental construction used in ozonation study is shown in Figure 2.7. Ozone gas was produced from air by PCI GLJ lab scale generator. Gas flowrate to the reactor was retained at 10 fr31h (283.2 l/h) and monitored using a rothameter incorporated with the generator. Ozone production was 13.3 g/h. Ozonation experiments were conducted using a sample of 1 liter in a 1.5 liter semi-batch bubble reactor with an functional depth of 23 em. Ozone gas was regaled at the underside of the reactor through a sintered glass plate diffuser. Two ozone traps including 2% potassium iodide solution (KI) were attached, with the aim of accumulating all residual ozone gas moving through the unreacted reactor. All experiments were processed at ambient temperature.

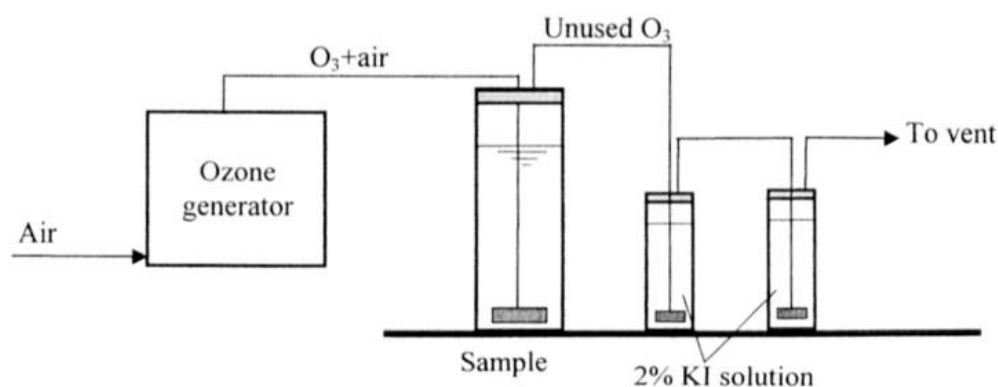


Figure 2.7: Experimental apparatus for ozone oxidation (Sevimli et al., 1999).

2.3.1.4 Color removal by lime (Sevimli *et al.*, 2000):

Processed on the effluent from WWTP 40 g/L lime was used to maintain 84% color and 57% COD removal.

2.3.1.5 Fenton oxidation process (Aydin *et al.*, 2002):

Executed on a lab scale biological reactor effluent with a COD of 650 mg/L and color of 4,950 Pt-Co. Optimum pH and interaction time were reported to be 4 and 30 minutes, relevantly. 200 mg Fe^{2+} /L and 400 mg H_2O_2 /L was used in integration to obtain %91.3 COD and %99.1 color removal.

2.3.1.6 Membrane technology (Koyuncu, 2003):

Membrane treatment is an extremely encouraging treatment method for contamination control of opium alkaloid processing from industry effluents. using nano-filtration (NF) and reverse osmosis (RO), full color removal and a 95% COD removal was reached on previously treated wastewater having COD = 950-2000 mg/L.

2.3.1.7 Anaerobic treatment (Özdemir, 2006):

Analysed opium alkaloid wastewater's anaerobic treatability and radiation pre-treatment's effect on anaerobic treatability. Reactor experiments were held in three UASB reactors (U1, U2, U3) for 138 days, continuously. U1 was only fed with opium alkaloid wastewater. U2 had 25 % (in terms of COD) calcium acetate co-substrate. U3 was fed with effluent of an acidification (SBR) reactor fed with alkaloid wastewater. Obtained removal efficiency was up to 78 % in U1 at initial COD concentration of 19 g/L (about 2/3 of original wastewater concentration). U2

was reported to show highest overall efficiencies (above 80 %) in all initial COD concentrations worked on (10, 15, 19 and 27.5 g/L).

2.3.1.8 Long-Term anaerobic treatability studies (Aydın et al., 2009):

The outcome of these experiments released that the effluents of opium alkaloid industry can be effectively treated by UASB type reactors at high rates of organic loading. More than 80% COD removal efficiency could be reached at high OLR's such as 10 kg COD/m³. day. The outcomes showed that anaerobic treatment can be carried out as a pretreatment to diminish the impact of high COD concentration on the occurring full-scale aerobic activated sludge process. Opium alkaloid industry wastewater's anaerobic treatment generates 300 L CH₄ per kg COD removed. In order to use anaerobic treatment as a pretreatment, daily methane production potential and its fuel oil coequal were quantified as 5000 m³/day and 2.35 ton/day, respectively. Using anaerobic pretreatment would remarkably reduce the production of sludge and requirement of energy before the aerobic treatment. As stated in this study, uncontrolled pollution of wastewater with the solvent N(Ndimethylaniline) had a serious interference effect on biological activity in the UASB reactor. A detailed toxicity work would be beneficial to distinguish inhibitors within the alkaloid industry raw effluents.

2.3.1.9 Chemical oxidation catalytic wet air oxidation (CWAO) process (Aytimur et al., 2010):

In CWAO experiments, the highest percentage of COD removal (35%) is obtained at 160°C and 1 g/L of catalyst loading, leading a COD value of 18155 mg/L. In the biological treatment experiments, COD value dropped to 3500 mg/L showing a total percentage COD removal of 88%. Comparing the two treatment methods, it is appeared that a single CWAO process is not efficient enough.

2.3.1.10 Anaerobic Digestion Model (Dereli et al., 2010)

The study showed the appropriateness of ADM1 for opium releasing effluents in the prophecy of effluent characteristics under a variety of operational conditions. The significant inconsistencies between simulations and biogas and methane flows in the subsequent periods of the experimental study are ascribed to a consistent fault related to the gas flow measurement system rather than the frailties of ADM1 model in the

prophecy of biogas flow at overcharged cases. Furthermore, sufficient results provided for effluent COD values throughout the whole study and consistency of it with biogas and methane flows during the earlier periods legitimized this argument. Figure 2.8 illustrates Lab-scale UASBR set-up.

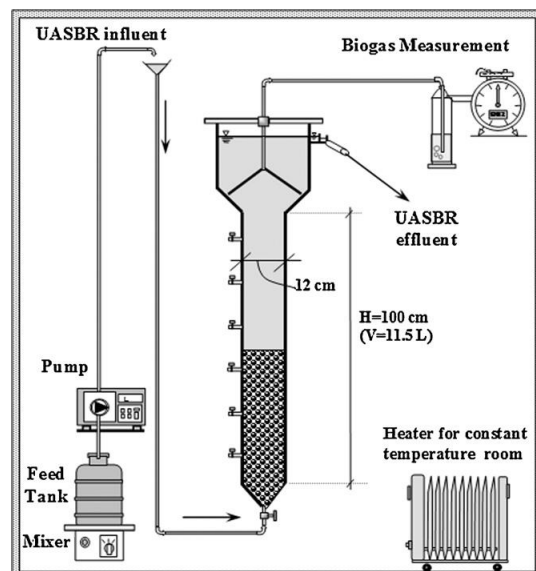


Figure 2.8: Lab-scale UASBR set-up.

2.3.1.11 Effect of gamma irradiation (Bural et al., 2010)

Wastewater that contains opium alkaloid with COD around 5000 mg dm^{-3} , which could be acquired by an anaerobic pre-treatment, can be affleuntly treated by aerobic SBR in combination with gamma irradiation. Radiation treatment upgrades the settling characteristics and supplies more compact sludge, which is judged as advantageous not only with regard to the true operation of SBR system but also with regard to handling of sludge. To the best of our knowledge, it is one of the first validations of such an effect of irradiation inaerobic biological wastewater treatment.

2.3.1.12 Solvent extraction separation of tyramine from simulated alkaloid processing wastewater by Cyanex 923/kerosene (Shen, 2013):

Transfer coefficients of experimental overall mass and tyramine recovery were obtained under the scale of hydrodynamic conditions in a handmade hollow fiber membrane contactor. Resistance based model prediction in series matched well with these experimental values for 50% TRPO/kerosene systems. Fractional analysis of resistance showed that rate-controlling step of mass transfer occurs on the aqueous phase. The results are useful for the design and scaling-up of the treatment process.

Table 2.5: Previous treatability studies on opium alkaloid wastewater

Method applied	Raw or treated waste water	Initial COD of wastewater (mg/L)	COD removal efficiency (%)	Process parameters	Reference
Anaerobic treatment (pilot)	Raw	13,000	45	$t_d = 2.5$ days, OLR = 5.2 kg COD/m ³ .day	Sevimli et al. (2000)
Anaerobic treatment (pilot)	Raw	7,000	70	$t_d = 2.5$ days, OLR = 2.8 kg COD/m ³ .day	Sevimli et al. (2000)
Anaerobic treatment (lab)	Raw	5,000	90	$t_d = 1.6$ days, OLR = 3.0 kg COD/m ³ .day	Sevimli et al. (2000)
Anaerobic treatment (lab)	Raw	8,000	87	$t_d = 1.6$ days, OLR = 5.0 kg COD/m ³ .day	Sevimli et al. (2000)
Anaerobic treatment (lab)	Raw	12,000	83	$t_d = 1.6$ days, OLR = 7.5 kg COD/m ³ .day	Sevimli et al. (2000)
Anaerobic treatment (lab)	Raw	14,400	68	$t_d = 1.6$ days, OLR = 9.0 kg COD/m ³ .day	Sevimli et al. (2000)
Anaerobic treatment (lab)	Raw	16,000	62	$t_d = 1.6$ days, OLR = 10.0 kg COD/m ³ .day	Sevimli et al. (2000)
Ozone oxidation	Effluent of WWTP	-	43	pH = 2.5, 40 minutes of ozonation	Sevimli et al. (2000)
Lime	Effluent of WWTP	2250	57	40 g/L lime	Sevimli et al. (2000)
Fenton	Effluent of lab scale reactor	650	91.3	pH = 4, Reaction time = 30 min, 200 mg Fe ²⁺ /L & 400 mg H ₂ O ₂ /L	Aydin et al. (2002)
Membrane (NF and RO)	Treated	950-2,000	95	-	Koyuncu (2003)
Alum	Effluent of WWTP	-	43	1000 mg/L alum pH = 6.5	Kınlı (1994)

Table 2.5: (continued)

Method applied	Raw or treated waste water	Initial COD of wastewater (mg/L)	COD removal efficiency (%)	Process parameters	Reference
FeCl ₃	Effluent of WWTP	-	41	1000 mg/L FeCl ₃ pH = 6.5	Kınlı (1994)
Fe ₂ (SO ₄) ₃	Effluent of WWTP	-	43	1000 mg/L Fe ₂ (SO ₄) ₃ pH = 6.5	Kınlı (1994)
Activated carbon	Effluent of WWTP	-	16	-	Kınlı (1994)
Perlite	Effluent of WWTP	-	15	-	Kınlı (1994)
Cement powder	Effluent of WWTP	-	10	-	Kınlı (1994)
Potassium perman ganate	Effluent of WWTP	-	45	1000 mg/L potassium permanganate	Kınlı (1994)
Hydrogen peroxide	Effluent of WWTP	-	7	20 mL/L H ₂ O ₂	Kınlı (1994)

Highest initial COD concentration used in these treatability studies was 16000 mg/L which is about half of the original alkaloid wastewater average COD value (30000 mg/L). Consequently, these studies could not be able to solve the problem completely.

2.4 Sludge Characteristics

In biological wastewater treatment part of COD removed is converted into biomass which will make up the biological sludge. The amount of sludge produce in the wastewater treatment plant, and should be directed to the sludge processing units can be expressed in terms of mass(g of total solids per day, dry basis) and volume (m³ of sludge per day, wet basis) (Androeli, 2007).

To express the characteristics of the sludge, as well as the production in terms of mass and volume, it is essential to have an understanding of some fundamental relationships. The following important items have been already presented:

- Relationship between solid levels and water content
- Expression of the concentration of dry solids
- Relation between flow, concentration and load
- Destruction of volatile solids
- Sludge density
- Solids capture
- Total, volatile and fix solids

Figure 2.9 illustrate the distribution of the solids according to these different forms.

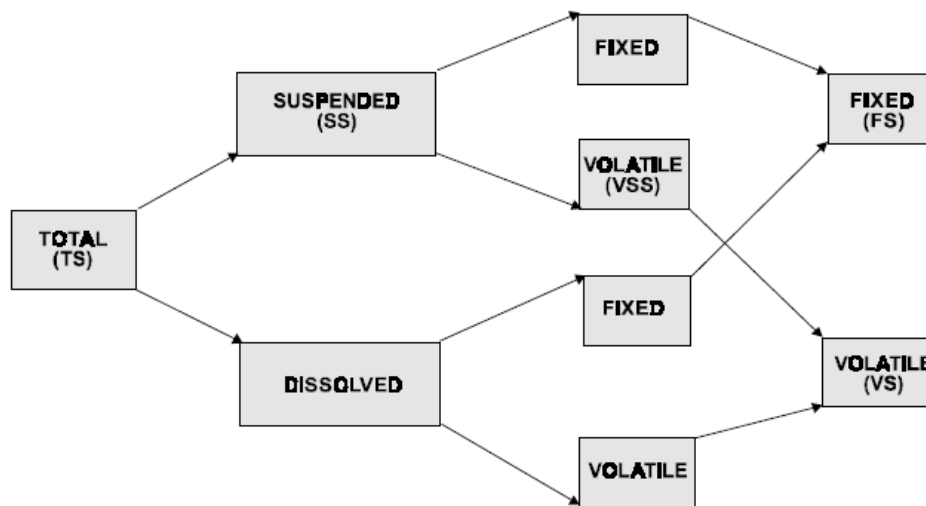


Figure 2.9: Sludge Solids distribution according to size and organic fraction (Luduvic, 2007).

2.5 Sewage Sludge Treatment

One of the most vital matters in environmental protection is sludge management. Great number of preservative measures and needed characteristics are specified in detail, both by international and local authorities for secure discarding of the excess sludge which resulted in wastewater treatment plants (Fytili et al., 2008; Insel et al., 2013). Demands contain practical stabilization conditioning operations before the disposal. Aerobic stabilization activity is one of the manageable options. It is executed either as a discrete operation or as linked to the biological treatment system processed as prolonged aeration scheme. While the future of TSS is notable for

evaluating the attainable dry solids content, it is essential to understand proper mechanisms during stabilization and this unavoidably includes the undergoing endogenous decompose process.

Sludge treatment procedures have variety of purposes that are intended for changing size qualities of the material to transform it into a form which is more appropriate for future reuse.

The objectives can be described as:

1. Convey it less abusive and lessen linked health hazards.
2. Lessen the volume of material (Birkett and Lester, 2003).

Options for sludge treatment includes preliminary operations, thickening, stabilization, conditioning, dewatering and drying processes. Figure 2.10 shows the unit operations and processes most commonly used for sludge treatment.

2.5.1 Sludge Stabilization

Sludge stabilization is one of the most favored and ordinarily used techniques for the sludge disposal. Stabilization process turns raw sludge into a less offensive form and leads to an efficient pathogen reduction, removal of organic matter as well as odor potential (Kim and Hao, 1990).

The pretreatment action will have been based upon the needs of this process that may also have been chosen for the manufacture of a product appropriate for a specific ultimate disposal routes, such as application on agricultural lands, incineration or other burning processes. These techniques are microbiological (aerobic or anaerobic) or chemical. When the action has not ended in a notable loss of water (e.g., through evaporation in composting) the ultimate product will be dewatered again in advance of final disposal. Contaminants inside raw sludge may be defiant and endure linked to solids. If so, then as the entire size of sludge is lessened during treatment, concentrations within the ultimate product will be more than in the raw material (Birkett and Lester, 2003).

Conventionally, operated sludge has been imprecisely clarified in terms of collective parameters such as total suspended solids (TSS) or volatile suspended solids (VSS); they could only be linked to an identically which simply stated the detected overall

diminish in the VSS content. A value of 0.05/d was frequently acquired for this coefficient (Marais et al., 1976).

Operated sludge is a commonly used biological wastewater system in various process configurations for organic carbon and nutrient removal (Taslı et al., 1997; Gernaey et al., 2004; Sarioglu et al., 2009; Raj et al., 2013). The process executes the deliberate task by also generating a side stream excess sludge – often called biological sludge, secondary sludge or biosolids – which required to be treated and discharged according to relevant regulations (Özdemir et al., 2014).

Operated sludge modeling presently allows for contemplating a multicomponent perspective for sludge stabilization by means of the death–regeneration mechanism introduced in ASM1 – the Activated Sludge Model No.1 (Henze et al., 1987). This mechanism galvanizes that a main part ($1 - f_{EX}$) of the decomposed biomass behaves as slowly biodegradable substrate, X_S , while the remaining (f_{EX}) gathers in the system as particulate microbial products, X_P ; X_S is subsequently altered into a soluble readily biodegradable substrate, S_S exploited by the active biomass, X_H (Orhon et al., 1989). This idea is also introduced and used in the explanation of sludge stabilization in latest studies, where particulate microbial products produced during endogenous decay, usually considered as inert in contemporary activated sludge models, were outlined to engaged in slow biodegradation under aerobic and anaerobic conditions (Lubello et al., 2009; Ramdani et al., 2010, 2012).

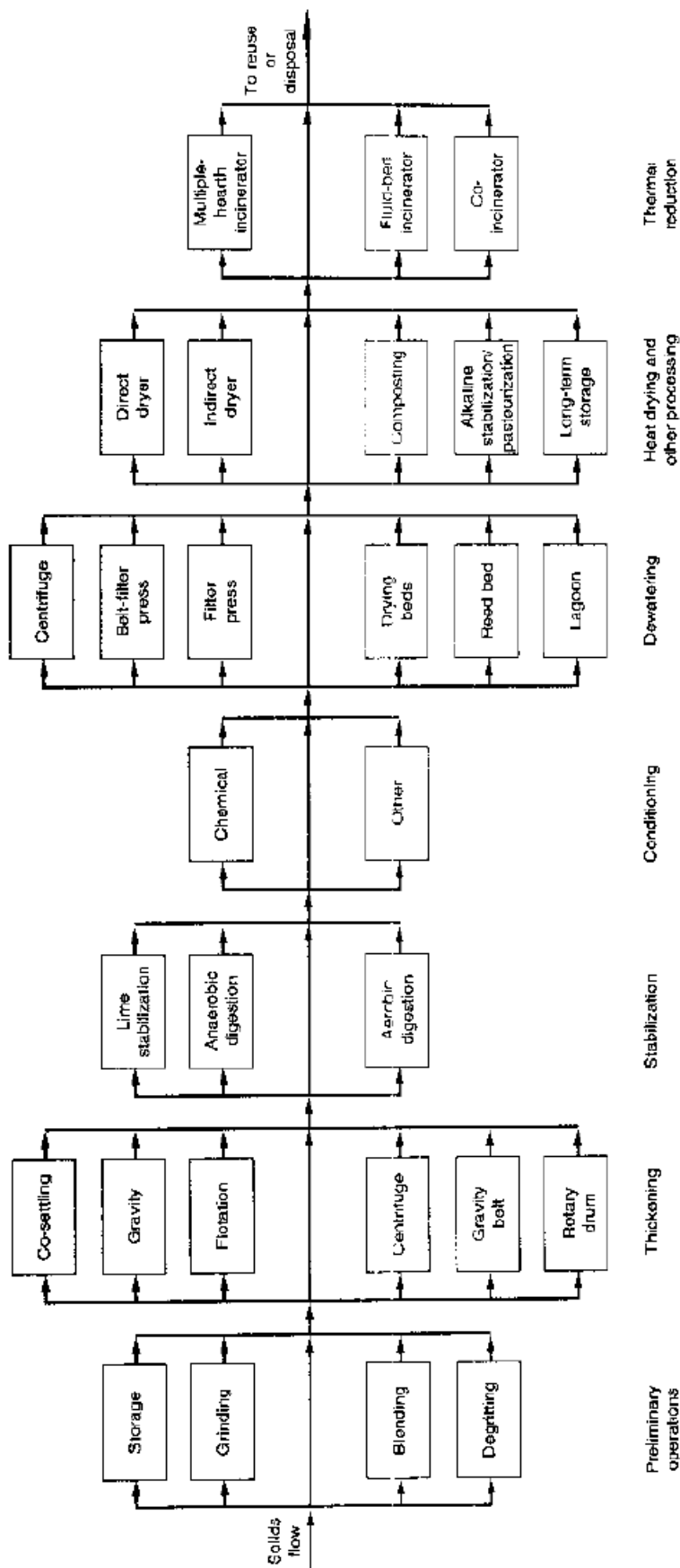


Figure 2.10: Sludge processing flow diagram (Metcalf and Eddy, 2003).

3. AEROBIC SLUDGE STABILIZATION

The term aerobic stabilization means the use of aerobic bioreactors to dissolve particulate organic matter derived from main simplification (predominantly biodegradable organic matter) and biological treatment of wastewater (predominantly biomass). By using either dissolved oxygen or nitrate-N, solids are oxidized as the terminal electron acceptor. The remnants includes primarily of a relatively inert (Leslie Grady et al., 1980).

It is notable that however the term "aerobic digestion" is not proper and the accurate term "aerobic stabilization" is entirely used in Europe, the term aerobic digestion is used here because of the application in North America (Erbes et al., 1980).

3.1 General Description

The biochemical modifications that occurred in an aerobic digester are shown in Figure 3.1. Biodegradable particulate organic matter is hydrolyzed and transformed into biodegradable soluble organic matter, unveiling nutrients such as ammonia-N and phosphate. The biodegradable soluble organic matter is then changed into carbon dioxide, water and active biomass through the operation of heterotrophic bacteria. The active biomass, in turn, engaging in decay, leading to the production of additional carbon dioxide and water, along with inactive biomass, i.e., debris (Leslie Grady et al., 1980).

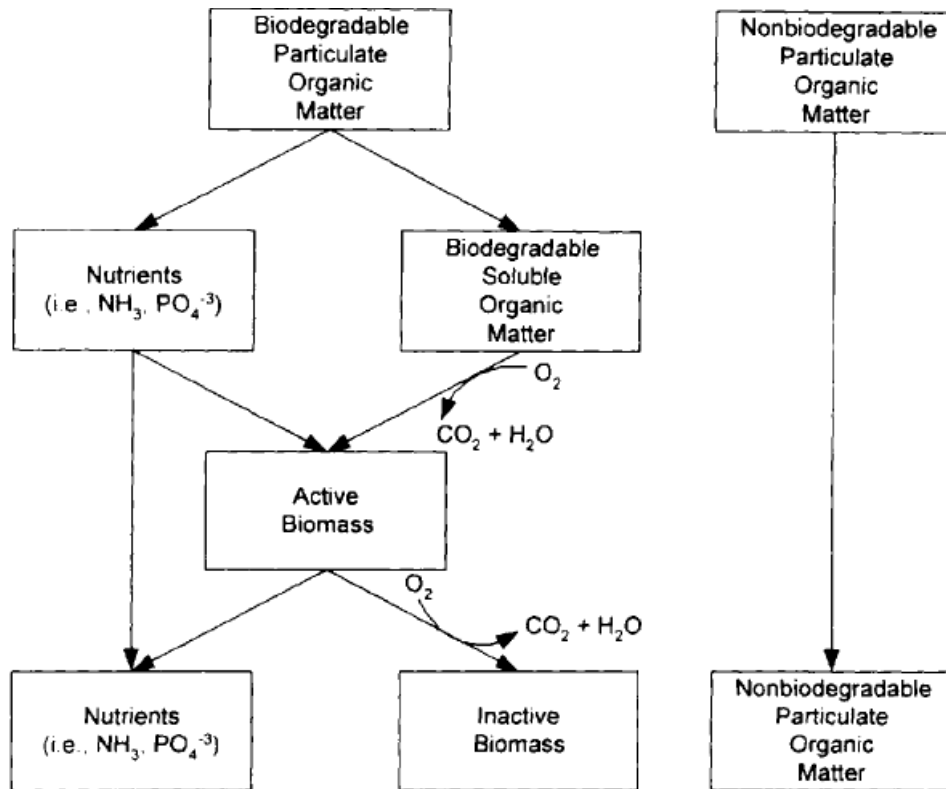
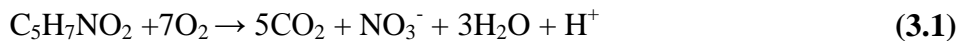


Figure 3.1: Schematic diagram of the events occurring during aerobic digestion (Leslie Grady et al., 1980).

3.2 Process Description

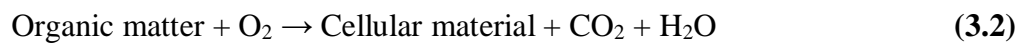
Aerobic digestion has a great resemblance to the activated sludge process. With the contribution of substrate interrupted, the microorganisms are imposed to devour their own energy reserves to survive. This is called endogenous phase, where in non-existence of food supply, the biodegradable cell mass is aerobically oxidized to carbon dioxide, ammonia and water. Ammonia is oxidized to nitrate during the reaction in line with the equation 3.1 (Andreoli et al., 2007).



It has been known for so long that once a microbial population has deployed occurring exogenous substrate to the level that there is deficient substrate to conserve the population, endogenous respiration begins. The population then lessens in mass and numbers. Aerobic digestion is projected to focus on waste cells and to lessen their numbers and mass via endogenous respiration (Erbes et al., 1980).

3.2.1 Microbiology

Municipal wastewater sludge's aerobic digestion is mostly strict to the principle, which is when there is insufficient external substrate available, microorganisms metabolize their own cellular mass. In real functioning, aerobic digestion includes the direct oxidation of any biodegradable matter and the oxidation of microbial cellular material by organisms. These paces are shown by the following reactions:



The process detailed by Equation 3.3 is allude to as endogenous respiration, which is basically the predominant reaction in aerobic digestion (Wang et al., 2009).

3.2.2 Advantages

Different number of advantages have been put in for aerobic digestion over other stabilization techniques, peculiarly anaerobic digestion. Derived from all present knowledge, the following advantages could be alluded to properly designed and activated aerobic digestion processes:

1. Have economical costs mostly lower than for anaerobic systems for plants under 5MGD (220 L/s)
2. Are comparatively easy to run compared to anaerobic systems
3. VSS is lessened to 40–50 percent, nearly parallel to that for anaerobic
4. Do not create unwanted odors
5. Will create a supernatant low in BOD₅, suspended solids, and ammonia nitrogen
6. Lessen the amount of oil in the sludge mass
7. A comparatively solid humus like end product is brought out
8. Lessen the quantity of pathogens to a lower level under normal design. Under auto heated thermopile design, most systems supply 100 percent pathogen dismantle.

3.2.3 Disadvantages

As with any procedure, there are also definite disadvantages. In aerobic digestion processes, the disadvantages are:

1. Generally create a digested sludge with very limited mechanical dewatering properties
2. Have high energy charges to supply oxygen, even for tiny plants
3. Are notably impacted in execution by temperature, location, and type of material inside the tank
4. Heavy metal cannot be removed
5. Absence of useful by-product (no methane).

3.3 Types of Aerobic Digestion

3.3.1 Conventional aerobic digestion

Conventional aerobic digestion aerates waste sludge for a prolonged period of time in unheated tanks, using air diffusers or surface aeration tools. The waste sludge that has been detached from the main biological activity is conveyed to the digester units, where the oxygen for microbial metabolism is supplied either by mechanical aerators or through a diffused aeration system (WEF, 2006).

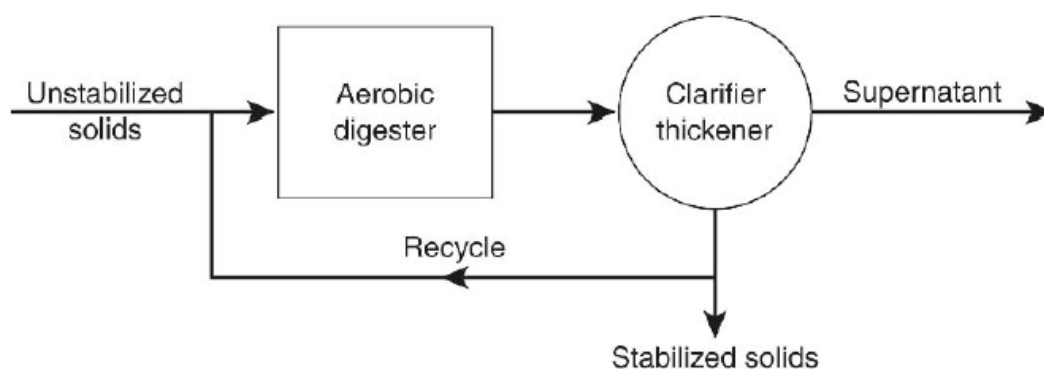


Figure 3.2: Flow diagram for a conventional aerobic digestion process (US EPA).

3.3.2 Aerobic digestion with pure oxygen

Aerobic digestion using pure oxygen is a alteration from the conventional aerobic digestion, in which oxygen in lieu of air is instantly provided to the medium. The

concentration of solids in the digester may be as high as %4 lacking any lessening in the oxygen transfer percentage to the biomass.

This procedure is appropriate for larger wastewater treatment plants, where locality is a chief factor, and in which oxygen is already being processed with a biological reactor. The feedback is highly exothermic, expanding the process productivity and favoring its use in cold-climate regions (Andreoli, 2007).

3.3.3 Thermophilic aerobic digestion

Thermophilic aerobic digestion includes aerating the sludge in a closed reactor with bacterial activity releasing heat. In point of the degradation activities occurring on recalcitrant organic amalgams, this process probably alike to the activated sludge process; nevertheless, higher temperatures included will end up a different population of bacteria. As well, processes usually operate at 45 to 70°C, 56 whilst Hudson (1996) signifies the process should reach 55°C for at least 4 hours with an overall time of 7 days. The system has been relevant to the stabilization of industrial SAS.126 Even though there isn't any large-scale studies about the future of EDCs in such processes, they have been exemplified to intensify the degradation of 2ethylhexyl phthalate in laboratory simulations using pronged sludge (Birkett and Lester, 2003). Figure 3.3 shows a schematic of ATAD (Authermal Thermophilic digestion).

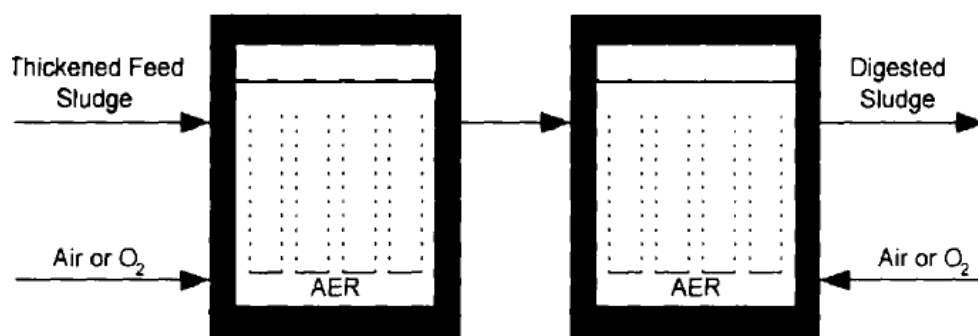


Figure 3.3: Autothermal aerobic digestion (Leslie Grady, 1980).

3.4 Kinetics of Aerobic Stabilization

3.4.1 Endogenous decay model

In aerobic digestion model of Marais and Ekama (1976), cell decay (loss of biomass) is based on endogenous decay model. This model originally described by McKinney (1958) concluded that cells contained an inert fraction which could not be biodegraded. X_H is oxidized to provide maintenance energy and the remaining part becomes inert endogenous mass or particulate inert organic products, X_P accumulating in the activated sludge system as shown in the Figure 3.4.

The rate of decrease in X is sum of the endogenous decay rate of X_H and the generation rate of X_P (Orhon and Artan, 1994).

$$\frac{dX}{dt} = \frac{dX_H}{dt} + \frac{dX_P}{dt} \quad (3.4)$$

The decrease of X_H to endogenous respiration is defined by first order rate expression:

$$\frac{dX_H}{dt} = -b_H X_H \quad (3.5)$$

Where b_H is endogenous decay rate

The rate of X_P production can be written as:

$$\frac{dX_P}{dt} = f_{EX} - b_H X_H \quad (3.6)$$

Where f_{EX} is inert fraction of the biomass

The consumption rate of dissolved oxygen in endogenous respiration phase can be expressed as:

$$\frac{dS_o}{dt} = -(1 - f_{EX})b_H X_H \quad (3.7)$$

S_o : dissolved oxygen concentration (mg O_2 /L)

3.4.2 Death-regeneration model

In this model, death or loss of viability of microorganisms (decay of heterotrophic biomass) is defined as (Orhon and Artan, 1994):

$$\frac{dX_H}{dt} = -b'_H X_H \quad (3.8)$$

where

b'_H : decay rate for heterotrophic organisms, d⁻¹

Inert endogenous mass, X_P is defined by following expression:

$$\frac{dX_P}{dt} = f_{PX} - b'_H X_H \quad (3.9)$$

A major part of nonviable biomass becomes available as slowly biodegradable substrate, X_S can be described by:

$$\frac{dX_S}{dt} = (1 - f_{PX}) - b'_H X_H \quad (3.10)$$

where

f_{PX} : inert fraction of the endogenous residue

Dold et al.(1980) and Warner et al. (1986) indicated that both concepts yield the similar results in aerobic systems. This can be shown by comparing the rates of X_P generation and oxygen utilization. From the Equation 3.10, the rate of X_H production from recycled substrate can be expressed as:

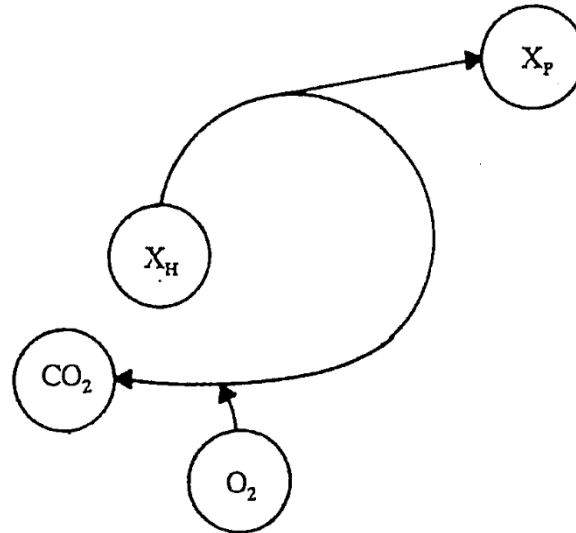
$$\frac{dX_H}{dt} = Y_H(1 - f_{PX}) - b'_H X_H \quad (3.11)$$

The oxygen consumption in this step is also given as:

$$\frac{dS_o}{dt} = -(1 - Y_H)(1 - f_{PX}) - b'_H X_H \quad (3.12)$$

The value of the $b'H$ coefficient is measured by using the death regeneration model in this thesis.

ENDOGENOUS DECAY MODEL



DEATH REGENERATION MODEL

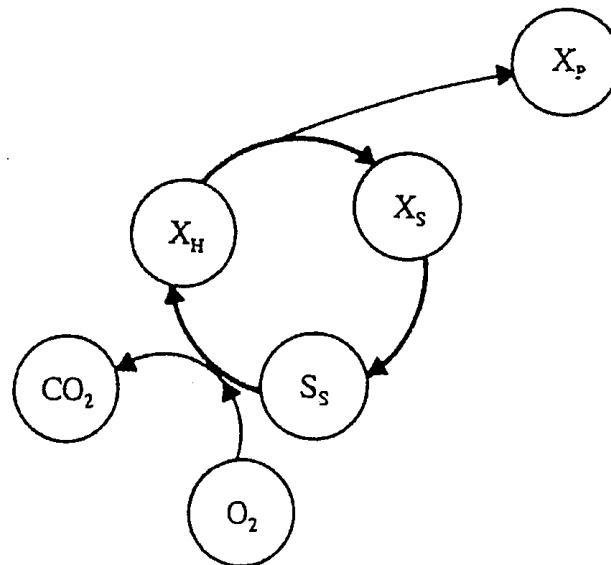


Figure 3.4: Schematic evaluation of endogenous decay and death-regeneration models (Orhon and Artan, 1994).

4. MATERIALS AND METHODS

4.1 COD Fractionation of Wastewater

COD fractionations of wastewater used for reactor feeding were in order to evaluate the effects of influent characteristics. Initial wastewater components as schematically shown in Figure 4.1 were calculated using following equations as defined by Orhon and Artan (1994):

$$C_{T1} = C_{S1} + C_{I1} \quad (4.1)$$

where

C_{T1} : total influent COD in wastewater

C_{S1} : initial total biodegradable COD

C_{I1} : initial total inert COD

$$C_{S1} = S_{S1} + S_{H1} + X_{S1} \quad (4.2)$$

where

S_{S1} : initial readily biodegradable COD

S_{H1} : initial rapidly hydrolysable COD

X_{S1} : initial slowly hydrolysable COD

$$C_{I1} = S_{I1} + X_{I1} \quad (4.3)$$

S_{I1} : initial soluble inert COD

X_{I1} : initial particulate inert COD

and

$$S_T = S_{S1} + S_{H1} + S_{I1} \quad (4.4)$$

where

S_T : total soluble COD

$$X_T = X_{S1} + X_{I1} + X_P \quad (4.5)$$

where

X_T : total particulate COD

X_P : particulate inert microbial products

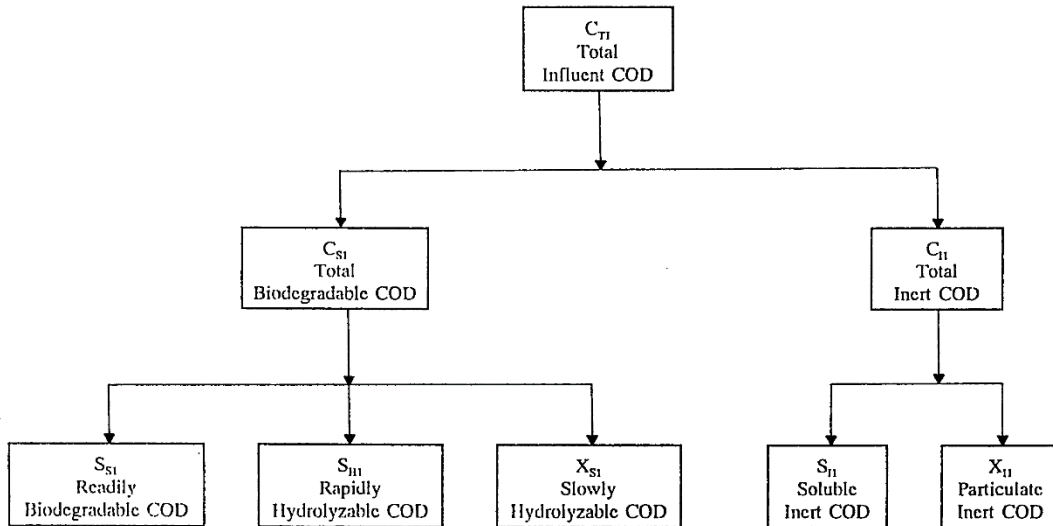


Figure 4.1: COD fractions in wastewater (Orhon and Artan, 1994).

4.1.1 Estimation of inert fractions for alkaloid wastewater

The assessment of the inert fractions present in industrial wastewater is very important because the inert fractions indicate indirectly the biodegradable COD fraction. Several methods have been proposed for the estimation of inert COD fractions in wastewater (Orhon et al., 2009).

Recent studies on the assessment of inert COD fractions were composed considering the generation of both particulate and soluble residual product. The majority of the methods proposed for the calculation of the initial particulate inert COD fraction in wastewater rely on simulations and experimental verifications using newly

developed multi-component activated sludge models (Henze et al., 1987; Orhon and Artan, 1994). Upon the recognition of the importance of residual microbial products for the assessment of inert fractions, Orhon et al (1994) proposed another procedure involving monitoring of the particulate inert products.

4.1.2 Reactor set-up

The experiment were started with the set up of two aerated batch reactors, the first one fed with raw wastewater sample, the second one with the soluble (filtered) wastewater sample, as previously suggested by Orhon et al., (1994). The batch reactors had working volume of 3L and seeded with minimal amount of biomass (150 mg/L) that had been acclimated in an aerated fill and draw reactor fed with wastewater sample,.Reactors were aerated continuously with the help of air diffusers and the oxygen concentration in the reactor kept above 2 mg/L to maintain aerobic conditions. Two mechanic stirrers were also provided with the reactor in order established well-mixed liquor in the system. The pH was kept in the range of 6.0-8.0, suitable for biological activity and the temperature was maintained at $20 \pm 1^{\circ}\text{C}$ during the operation of parent reactors. Evaporation losses were made up with distilled water every day.

Additionally for the nutrient requirements of activated sludge, solution that is composition of 160 g/L KH_2PO_4 , 320g/L K_2HPO_4 was added to the reactor. In the reactor, the amount of solution was adjusted to supply 10mL of solution for 1000mg COD/L of carbon source (O'Connor, 1972).

4.1.3 Experimental procedure

Total COD is 27344 mg/L, Soluble COD is 23474 mg/L is diluted and the reactors were started with an initial wastewater total COD of 1400 mg/L, soluble COD of 1174 mg/L and they were observed for 38 days. 25 mg/L VSS is added to raw wastewater reactor. The experiment was continued until all biodegradable COD is depleted and the biomass is mineralized. The experiment was ended when subsequent samples have the same unchanging COD values.

The experiment is based on the measurement of following COD values:

C_{T1} : total wastewater COD fed in the raw wastewater reactor

S_{T1} : total soluble wastewater COD fed in the filtered wastewater reactor

$(C_T)_1$: final total COD of raw wastewater reactor

$(C_T)_2$: final total COD of filtered wastewater reactor

$(S_T)_1$: final soluble COD of raw wastewater reactor

$(S_T)_2$: final soluble COD of filtered wastewater reactor

At the beginning of the experiment:

$$C_{T1} = C_{S1} + S_{I1} + X_{I1} \quad (4.6)$$

At the end of the experiment, by assuming that CS and XH= 0,

$$(C_T)_1 = (S_P)_1 + S_{I1} + (X_P)_1 + X_{I1} \quad (4.7)$$

where

$(X_P)_1$: residual particulate microbial products generated in raw wastewater reactor

$(S_P)_1$: residual soluble microbial products generated in raw wastewater reactor

and,

$$(S_T)_1 = (S_P)_1 + S_{I1} \quad (4.8)$$

The total COD removed in the first reactor

$$(\Delta C_T)_1 = C_{T1} - (C_T)_1 \quad (4.9)$$

In the second reactor fed with S_{T1} , initially,

$$S_{T1} = S_{S1} + S_{I1} \quad (4.10)$$

At the end of the experiment,

$$(C_T)_2 = (S_P)_2 + S_{I1} + (X_P)_2 \quad (4.11)$$

where

$(X_P)_2$: residual particulate microbial products generated in filtered wastewater reactor

(S_P)₂: residual soluble microbial products generated in filtered wastewater reactor

The total COD removed in the second reactor:

$$(\Delta C_T)_2 = S_{T1} - (C_T)_2 \quad (4.12)$$

The initial inert particulate COD, X_{I1}:

$$X_{I1} = [(C_T)_1 - (S_T)_1] - [(C_T)_2 - (S_T)_2] \frac{(\Delta C_T)_1}{(\Delta C_T)_2} \quad (4.13)$$

Assesment of particulate inert COD fraction to total COD, f_{XI}:

$$f_{XI} = X_{I1}/C_{T1} \quad (4.14)$$

The initial inert soluble COD, S_{I1}:

$$S_{I1} = (S_T)_1 - \frac{(S_T)_1 - (S_T)_2}{1 - ((\Delta C_T)_2/(\Delta C_T)_1)} \quad (4.15)$$

Assesment of soluble inert COD fraction to total COD, f_{SI}:

$$f_{SI} = S_{I1}/C_{T1} \quad (4.16)$$

4.2 Assesment of Aerobic Sludge Stabilization

4.2.1 Reactor set-up

The sludge sample was taken from aerobic membrane bioreactor of the wastewater treatment plant. The study was carried out at a alkaloid treatment plant with a capacity of 480 m³/day. The sludge sample was brought to the laboratory and aerated.

Aerobic sludge stabilization assays were initiated in 6 L cylinder reactor with a working volume of 3 L at 20±0.5 °C. The pH of the reactors was maintained at 7±0.5. The aerobic stabilization experiment was started with an initial SS concentration of 23000 mg/L and a VSS concentration of 9800 mg/L. During the aerobic stabilization period, the dissolved O₂ concentration in the reactors was kept

above 2 mg/L using air stones. Evaporation losses were made up with distilled water every day.

4.2.2 Experimental procedure

Sludge that includes 23000 mg SS/L were used in the process of Aerobic Stabilization. SS, VSS and pH measurements were made timely and daily. The experiments had been carried on until the SS/VSS parameters were stabilized. The experiments had taken approximately 19 days. The AQUASIM simulation program was used in the modelling processes. Decay of the particulate substance study was based on (Özdemir et al., 2014)

4.2.3 Modelling studies

The experimental data monitored throughout the stabilization period was evaluated using a different model based on death-regeneration mechanism as defined in ASM1 (Henze et al., 1987). The structure of ASM1 is better suited for microbial environments with no external substrate such as sludge stabilization, as it defines a sequential mechanism of death; cellular decay; hydrolysis of non viable cellular material into soluble biodegradable substrate and microbial products; and finally microbial growth on generated soluble substrate. Reuse of cellular material for cryptic growth is a commonly suggested mechanism in sludge stabilization: Stabilization under starvation conditions triggers cell disintegration and lysis after microbial death; this way, cellular material is recycled and through hydrolysis, it becomes available for the growth of the surviving fraction of the microbial culture. Consequently, the basic template of ASM1, which provides a mechanistic description for this process is adopted in this part of the study. Its structure was slightly modified to include partial/slow hydrolysis of the particulate microbial products, X_p and biodegradation of the hydrolysis products, as observed in similar studies on sludge stabilization (Lubello et al., 2009; Ramdani et al., 2012). Simulations were conducted with Aquasim software (Reichert et al., 1998). The mechanistic structure of the model is given Table 4.1.

Table 4.1: Matrix representation of the model structure adopted for the assessment of biomass fractions

Component	S_S	X_I	X_S	X_H	X_P	S_O	Process rate $ML^{-3} T^{-1}$
Process							
Aerobic Growth of heterotrophs	$-\frac{1}{Y_H}$			1		$-\frac{1 - Y_H}{Y_H}$	$\mu_H \cdot \frac{S_S}{K_S + S_S} \cdot X_H$
Decay of heterotrophs			$1 - f_{EX}$	-1	f_{EX}		$b_H X_H$
Hydrolysis of X_S	1		-1				$k_{hX} \cdot \frac{X_S/X_H}{K_{XX} + X_S/X_H} \cdot X_H$
Hydrolysis of X_P	1				-1		$k_{XP} \cdot \frac{X_P/X_H}{K_{XP} + X_P/X_H} \cdot X_H$
Parameter, ML^{-3}	COD	COD	COD	Cell COD	COD	O_2	

The biomass measured in VSS units was converted to COD and fractionated by considering four particulate organic components: X_H , X_I , X_S , and X_P to quantify sludge production. For assessment of these particulate COD components during stabilization process, the following expressions were used (Orhon and Artan, 1994).

X_H concentration:

$$\frac{dX_H}{dt} = -b_H X_H \quad (4.17)$$

where

X_P concentration:

$$\frac{dX_P}{dt} = f_{EX} b_H X_H - k_{XP} \left(\frac{X_P/X_H}{K_{XP} + (X_P/X_H)} \right) X_H \quad (4.18)$$

X_S concentration:

$$\frac{dX_S}{dt} = k_{hX} \left(\frac{X_S/X_H}{K_{SX} + (X_S/X_H)} \right) X_H \quad (4.19)$$

X_I concentration:

$$X_I = X_{I1} \frac{\theta_X}{\theta_h} \quad (4.20)$$

In this case, amount of total sludge, X_T in the stabilization reactors was calculated as:

$$X_T = X_H + X_P + X_S + X_I \quad (4.21)$$

4.2.4 Respirometric assesment of endogeneous decay

Respirometric assessment of endogenous decay rate, b_H was conducted in accordance with a procedure proposed by (Ekama et al., 1986). In this method, the endogenous respiration rate, b_H , is determined by monitoring changes in the oxygen uptake rate (OUR) profile of a continuously aerated sludge sample without any addition of external substrate. Relevant basis for evaluation may be defined as follows: The decrease in active heterotrophic biomass, X_H , with time is expressed as in Eq. 4.22.

$$X_H = X_{H0} e^{-b_H t} \quad (4.22)$$

On the other hand, OUR corresponding to endogenous decay monitored in the experiment may be assessed by Eq. (4.23):

$$OUR = (1 - f_E) b_H X_H \quad (4.23)$$

where f_E is the total endogenous residue, i.e. soluble and particulate microbial products released during endogenous decay. A relationship between $\ln OUR_t$ and b_H given in Eq. (4.24) may be obtained by rearranging expressions 4.22 and 4.23:

$$\ln OUR_t = [\ln(1 - f_E)b_H X_{H0}] - b_H t \quad (4.24)$$

Consequently, by plotting $\ln OUR$ vs. time, the slope of the OUR curve yields the value of the endogenous decay coefficient, b_H .

4.2.5 Respirometric assessment of microbial activity

The study also utilized another respirometric procedure, which evaluates endogenous decay based on loss of activity and viability of heterogenic biomass in the sludge based on the method defined by (Orhon et al., 1998). The method relies on assessing change in the measured OUR values as a function of $\mu_H X_H$, which determines the magnitude of the initial OUR level. The method is designed to maintain a constant level for μ_H and this way, it allows calculating the variation of X_H with time during aerobic stabilization. Related evaluation is based on the assumption that the initial OUR in a batch reactor operated with sufficient/ excess substrate sustains maximum growth conditions. A constant amount of readily biodegradable substrate is added in successive intervals and corresponding initial OUR plateaus are defined by Eq. 4.25:

$$OUR_t = \left[\frac{1 - y_H}{Y_H} \mu_H + (1 - f_E)b_H \right] X_{H0} e^{-b_H t} \quad (4.25)$$

Linearized version of the above equation (see Eq. (4.26)), yields the corresponding b_H value, as the slope of the $\ln OUR$ plot.

$$\ln OUR_t = \ln \left[\frac{1 - y_H}{Y_H} \mu_H + (1 - f_E)b_H \right] X_{H0} - b_H t \quad (4.26)$$

4.3 Analytical Procedure

COD measurements were performed according to ISO 6060 (1986). For determination of soluble COD, samples were filtered by use of 0.45 μm membrane filters.

Liquid samples were periodically taken to monitor SS, VSS, and pH. SS and VSS measurement were carried out after filtration of the sample from Millipore AP40 glass fiber filters with an effective pore size of approximately 1.2 μm . SS and VSS analysis were performed as described in Standard Methods (APHA).

For the determination of bH, according to the method proposed by (Echama et al., 1986) sludge samples were withdrawn at 5-min daily intervals from the aerobic stabilization reactor and the oxygen electrode was directly placed in the measurement flasks. Dissolved oxygen (DO) measurements were conducted using WTW type oxygenmeter.

The AQUASIM simulation software was used for the implementation and calibration of the model (Reichert et al., 1998). Model calibration was implemented by means of an iterative calibration protocol, involving manual calibration of model components in each iteration step and fitting all the model outputs on real time data (Insel et al., 2003).

5. RESULTS AND DISCUSSION

5.1 Evaluation of Batch Experiments For Inert Fractions

Inert COD fractions of alkaloid wastewater were experimentally determined as defined by Orhon et al., (1994). Experimental results are represented in Table 5.1.

Table 5.1: Experimental results for alkaloid wastewater sample

Time(day)	Raw wastewater reactor (1st Reactor)		Filtered wastewater reactor (2 nd Reactor)	
	Total COD (mg/l)	Soluble COD (mg/l)	Total COD (mg/l)	Soluble COD (mg/l)
0	1400	1174	1210	1174
1	790	668	750	664
2	505	472	500	458
3	342	315	365	352
10	135	118	210	126
24	140	118	135	119
31	140	118	115	105
38	145	118	115	105

Table 5.2: Experimental results related to inert COD fractions of the wastewater

Parameter	Value (mg/L)
Raw wastewater reactor	
C_{T1}	27344
$(C_T)_1$	2900
$(S_T)_1$	2360
Filtered wastewater reactor	
S_{T1}	23474
$(C_T)_2$	2300
$(S_T)_2$	2100

Results of inert COD experiment are given in Table 5.2 and Figure 5.1 and 5.2. From the Equation 4.13 and 4.15, concentrations of X_{II} and S_{II} were calculated as 309 mg/L (1.13 % of the C_{TI}) and 416 mg /L (1.52 %).

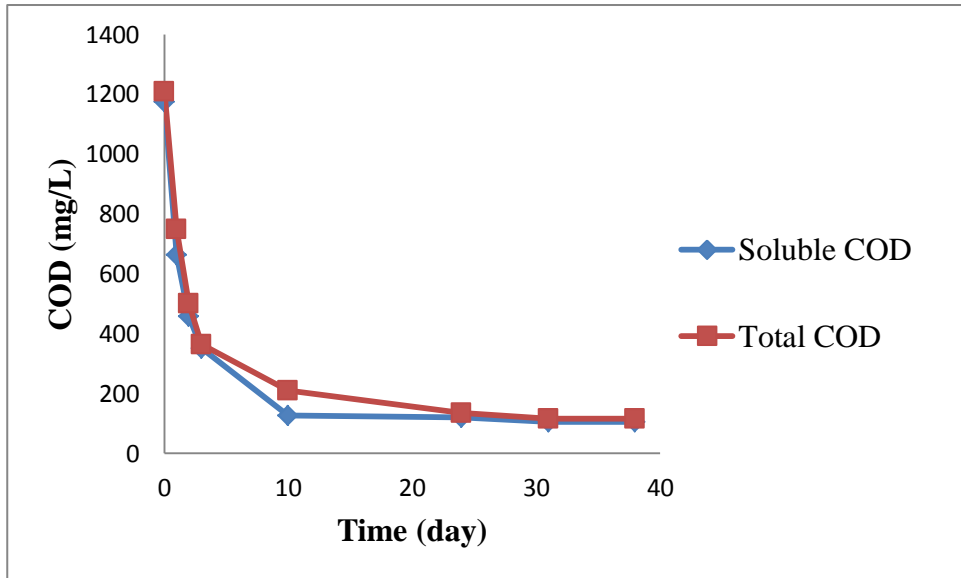


Figure 5.1: Total and soluble COD results obtained for filtered wastewater reactor

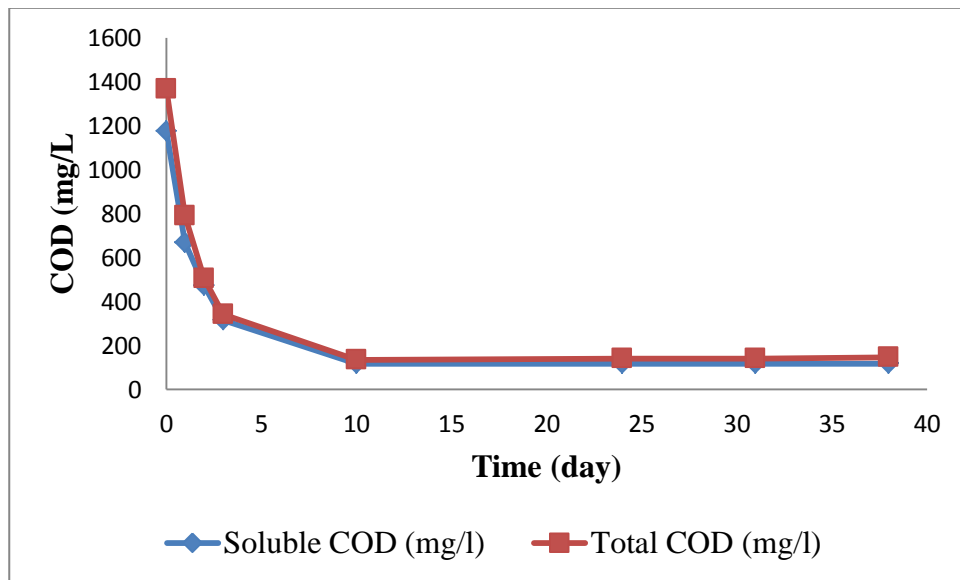


Figure 5.2: Total and soluble COD results obtained for raw wastewater reactor

5.2 Evaluation of Aerobic Sludge Stabilization

The aerobic stabilization experiment was started with initial VSS concentration of 23000 mg/L and a VSS concentration of 9800 mg/L. As shown in Fig. 5.3., the

effective decrease in SS and VSS level could only be observed within the first 3 d. The VSS/SS ratio of the stabilized sludge was found 0.35 mg VSS/mg SS. External aerobic sludge stabilization of the thickened sludge achieved a volatile suspended solids reduction 38% after 19 days as illustrated in Fig. 5.4.

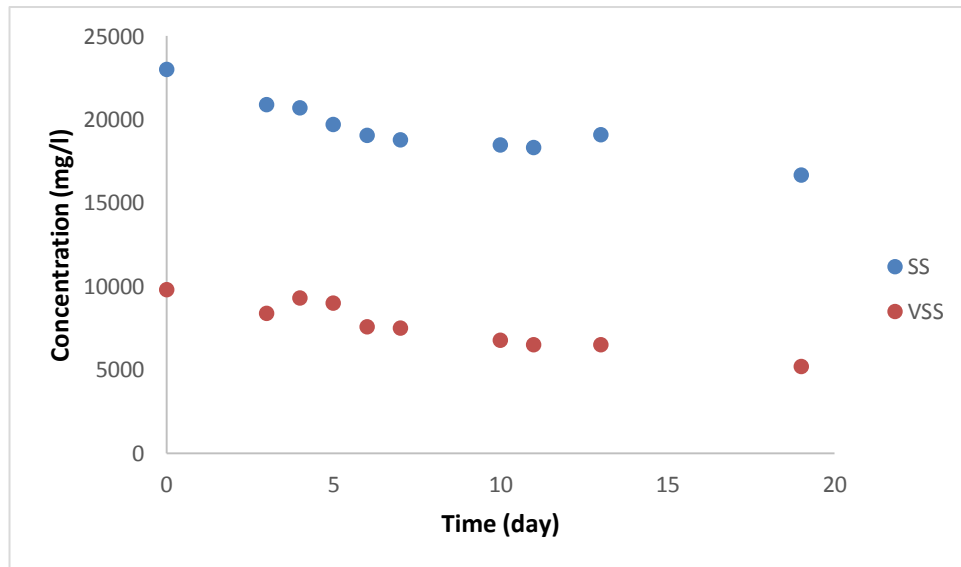


Figure 5.3 : SS VSS profile during aerobic stabilization

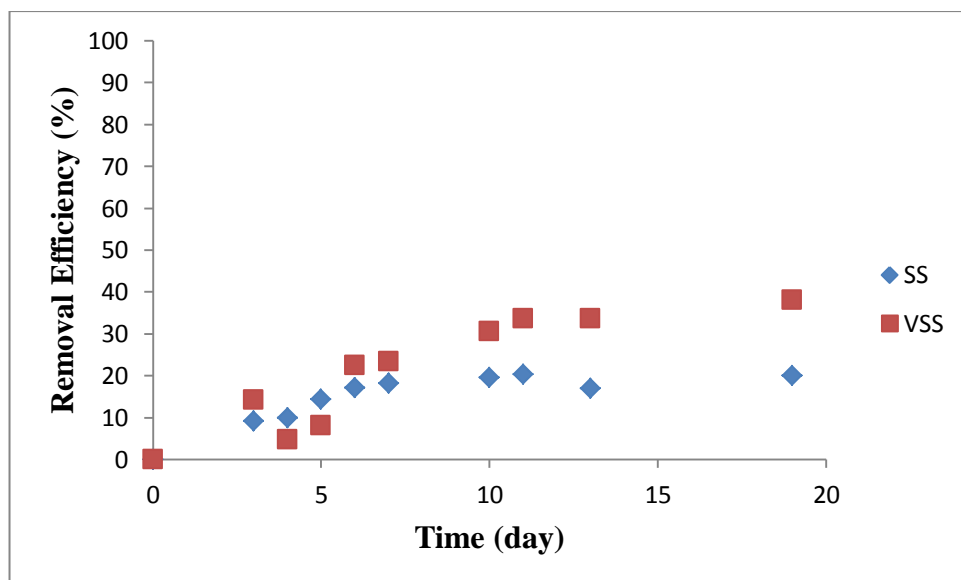


Figure 5.4: Observed solids reduction during aerobic stabilization

5.3 Respirometric Assesment of Aerobic stabilization

The determination of the kinetics of decomposition of industrial wastewater and aeration system design-related parameters to determine respirometric techniques are widely used. (Insel et al., 2003; Cokgor et al., 2008). Activated sludge samples from the MBR pilot unit were delivered to İstanbul Technical University, Environmental Engineering, Sedat Üründül Biotechnology Labarotory and were subjected to biomass activity test in an oxygenated environment. Biomass were placed on an Applitek RA-1000 continuous respirometer cell type and on which addition of raw Alkaloid wastewater (100 mL initial COD: 31,000 mg/L) was performed and oxygen utilization rate against time (OUR) was recorded at a frequency in a minute. Mixture of biomass - wastewater was chosen to reflect F/M (Food/Microorganism=0.25 kg COD/kg MLSS/day) ratio in pilot treatment plant. In order to adjust F/M ratio, MBR sludge was set to level of 2900 mg MLSS/L by using pilot MBR water. Respirometrical calculations under the batch conditions are shown in Fig. 5.5.

It was observed that when wastewater is added on biomass in an aerobic environment, OUR level increases rapidly from 35 mg O₂/L/hour to 365 mgO₂/L/hour in a couple of minutes (Process Heat=30°C; MLSS= 2900 mg/L; Dissolved Oxygen=6 mg O₂/L). Oxygen used per a unit of MLSS could be calculated as 126 mg O₂ /L/gMLSS/hour. It can be understood from the respirometric profile in Fig. 5.5 that 85 percent of the organic material in raw wastewater is readily biodegradable and it is not inhibited in an aerobic environment.

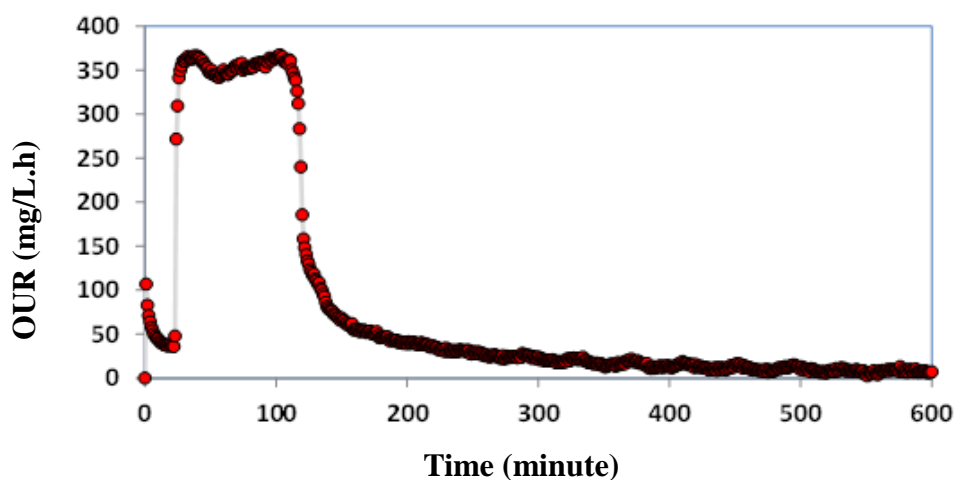


Figure 5.5: Model simulation of the OUR profile (SRT:20 days)

5.4 Assessment of Heterotrophic Endogeneous Respiration Rate Under Aerobic Conditions

Application of the method proposed by (Ekama et al., 1986) based on successive measurements of descending OUR levels in the course of sludge stabilization yielded b_H value of 0.14/d, with an equally reliable statistical confidence reflected by $R^2 = 0.9736$ as plotted in Fig. 5.6.

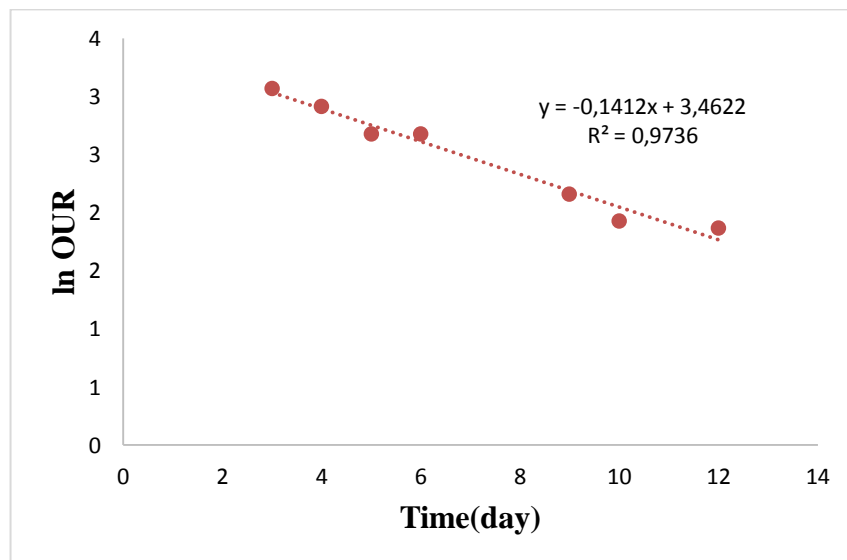
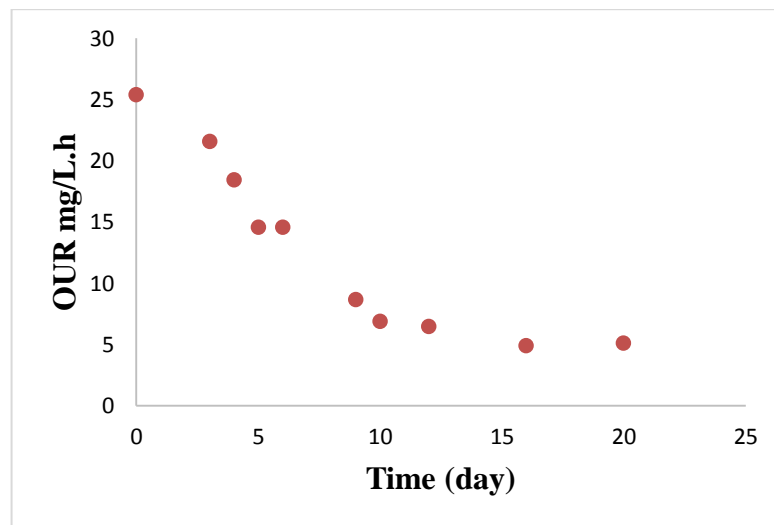


Figure 5.6: Figure Assessment of the endogenous decay coefficient based on successive OUR values.

5.5 Modelling of Experimental Results

5.5.1 Biomass fractionation

Biomass composition assessed by model calibration involves four major fractions, namely heterotrophic active biomass, X_H ; remaining particulate slowly biodegradable COD, X_S ; particulate inert COD of influent origin, X_I and particulate metabolic products, X_P generated in the course of metabolic reactions in the reactor.

This way, biomass can be defined in terms of total particulate COD, X_T reflecting all defined components, aside from the conventional VSS parameter, X_{VSS} . Table 5.3 outlines these biomass components resulting from model calibration together with a similar biomass fractionation obtained for the operation of the same fill and draw reactor at sludge age of 10 days, as reported in the previous part of the study (Ozdemir et al., 2014). It indicates a total solids concentration of mg COD/L when expressed in terms of cell COD, corresponding to a VSS value of 2375 mg/L; the corresponding active biomass (X_H) level is around 2854 mg COD/L.

Table 5.3: Assessment of appropriate values for biomass fractions.

Symbol	Parameters	Value	Units
X_H	Active heterotrophic biomass	2854	mg COD/L
X_S	Slowly biodegradable COD	0	mg COD/L
X_P	Maximum hydrolysis rate for X_P	981	mg COD/L
X_I	Hydrolysis coefficient for X_P	228	mg COD/L
X_T	Total biomass	4063	mg COD/L
X_F	Fixed biomass	100	mg COD/L
X_{VSS}	Total biomass	2861	mg VSS/L

It appears that “stabilization” commonly referred to in the extended aeration configuration of the activated sludge process decreases the relative magnitude of active microbial community, while accumulating inert solids in the wastewater and particulate metabolic products.

Table 5.4: Model parameters for the aerobic stabilization process

Symbol	Parameters	Value	Units
K_{hX}	Maximum hydrolysis rate for X_S	0.6	d^{-1}
K_{XX}	Hydrolysis coefficient for X_S	0.03	mg COD/mg COD
K_{hP}	Maximum hydrolysis rate for X_P	0.02	d^{-1}
K_{XP}	Hydrolysis coefficient for X_P	0.01	mg COD/mg COD
b_{DR}	Microbial decay rate	0.14	d^{-1}
f_{EX}	Particulate residue of X_H	0.15	-

The model calibration of solids profile obtained during stabilization expressed in terms of COD was plotted in Figure 5.7.

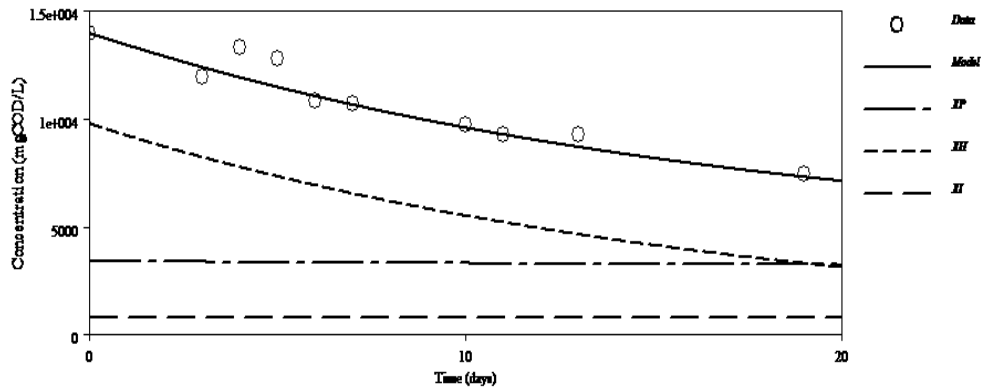


Figure 5.7: Model calibration of the sludge profile and simulation of particulate fractions during stabilization.

5.5.2 Fate of the particulate cod fractions of sludge

The determined wastewater characteristics were used in ASM1 (Henze et al., 1987) modified for endogenous respiration (Orhon and Artan, 1994) to define particulate COD fractions of sludge for selected SRT. The model parameters determined by means of OUR calibration in Table 5.5.

Table 5.5: Assesment of appropriate values for model coefficients and biomass fractions.

<i>Parameters</i>	<i>Value</i>
b_H	0.2 d-1
maximum growth rate, μ_H	4 d-1
Half saturation coeffieint K_S	10 mg COD/L
Maximum hydrolysis rate, K_{hX}	2.1 d-1
Hydrolysis half saturation coefficient, K_{XX}	0.024 d-1
Heterotrophic yield coefficient, Y_H	0.58 g cell COD/ g COD
<i>Biomass fractions</i>	
Active heterotrohic biomass, X_H	3700 mg COD /L
Slowly biodegradable COD, X_S	532 mg COD/L

Table 5.6 reflects the significant difference in the biomass composition inflicted by the sludge age of the biological reactor. Sludge age did not only the change the composition of the biomass but also, the biodegradation characteristics of sewage used as the organic substrate to generate the sludge for the study. The variable nature of the kinetics for the hydrolysis of slowly biodegradable fractions are shown in Table 5.6.

Table 5.6: Variable process kinetics as a function of different sludge age (Ozdemir, et al., 2014).

<i>Parameters</i>	<i>Unit</i>	$\theta_X=2$ days	$\theta_X=10$ days	$\theta_X=20$ days
Maximum hydrolysis rate for X_P , k_{hP}	d^{-1}	-	0.012	0.04
Hydolysis coefficient rate for X_P , K_{XP}	mg COD/ mg COD	-	0.01	0.01

Activated sludge processes operated at different sludge ages have differen K_{XP} . K_{XP} value increased with increasing SRT.

6. CONCLUSIONS

The objective of this study was to evaluate the biological characterization and sludge stabilization of alkaloid wastewater. At the same time all kinetics and stoichiometric coefficients were determined about this biological aerobic system. For this purpose, two fill and draw reactors were conducted to determine the COD fractions of wastewater.

Experimental studies involved assessment of aerobic stabilization process by conventional methods, molecular techniques and respirometric analyses. Experimental data were simulated in terms of ASM1 model.

Stabilization process is likely to result in cellular death and lysis organic microbial residues which may serve as additional endogenous substrate for the remaining viable biomass. Consequently, this mechanism would be better interpreted in terms of a death-regeneration model.

The VSS removal rate during aerobic stabilization of alkaloid sludge. It was observed that after aerobic stabilization VSS reduction is 38% and SS reduction is 20%.

Model evaluation based on death generation mechanism indicated a gradually decreasing decay rate for solid; the first phase could be associated with the inactivation/death of the viable biomass and the second controlled by the slower break down of particulate metabolic product.

X_p is important for organic carbon removal. Model evaluation indicated that it was possible to hydrolyse the microbial products X_p generate at slow rate during endogenous respiration.

Earlier studies on aerobic and anaerobic digestion of activated sludge investigated the design and optimization of process aimed at stabilizing the active heterotrophic biomass X_H fraction of the activated sludge. However there is serious gap for the effect of these processes on the degradation of each organic fraction of the sludge.

Furthermore, it is generally considered that the inactive organic fractions of the sludge are not biodegradable under aerobic or anaerobic digestion conditions.

This study will also be beneficial for the design of Afyon Alkaloid Industrial Wastewater Treatment Plant.

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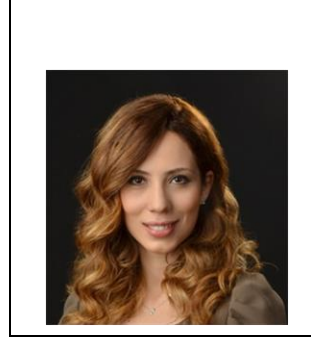
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